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**High Nitrogen Explosives. Part 1. 2,6-Dinitropyridines  
and Dibenzo-1,3a,4,6a-Tetraazapentalenes**

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# Naval Air Warfare Center Weapons Division

## FOREWORD

The Navy continues to have a need for dense powerful but insensitive explosive and propellant ingredients, which may be satisfied by developing new high nitrogen materials. This report documents research towards the synthesis of polyaminopoly-nitropyridine-1-oxides and dibenzo-1,3a,4,6a-tetraazapentalenes.

This interim report covers work supported by the Office of Naval Research and performed over the period of October 1992 through February 1994. This report has been reviewed for technical accuracy by Richard A. Hollins.

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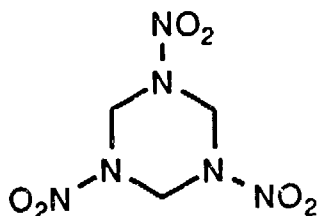
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## INTRODUCTION

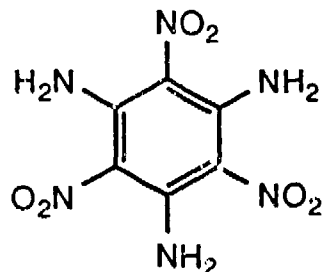
The Navy's ongoing requirement for explosives and propellants of superior performance to enable missile systems to defeat ever more demanding targets, at longer and longer range, is self-evident. This requirement has led to a number of productive programs to devise and synthesize new dense energetic ingredients with enhanced performance as explosives or propellant oxidizers. Notable among these are hexanitrobenzene, CL-20, tetranitrocubane and, more recently, ammonium dinitramide. This requirement also led to the development of new energetic polymers, which have been used as binders for both explosive and propellant formulations (Reference 1).

Equally apparent is the simultaneous need for more insensitive explosives and propellants to decrease the hazards for, and increase the reliability of, both personnel and equipment in an increasingly hostile environment, but without impairing the performance of the weapons systems. Principal among the inadvertent stimuli to which an item of ordnance may be subjected during manufacture, handling, storage, transport, testing, use, and disposal are various levels of heat, impact, friction, electrostatic discharge and shock, and any combination thereof. The Insensitive Munitions Advanced Development (IMAD) program has addressed this difficult problem; but has largely been restricted to manipulation of formulations using existing proven ingredients and to engineering solutions specific to the particular weapon system in question. The overriding philosophy is to ensure that the weapon "fails safe." Such approaches must be self-limiting, and there is, therefore, a need for new insensitive ingredients, particularly those which can endure environmental abuse and still function as required at the target. One specific requirement for use in deformable or penetration warheads is a dense explosive matching the explosive performance of cyclotrimethylenetrinitramine (RDX) with the stability and insensitivity of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). Specifically, a material is required which combines the detonation velocity and pressure of RDX with the chemical stability and explosive insensitivity of TATB.



RDX

Density 1.80 (1.83) g/cm<sup>3</sup>  
 VofD 8940 m/s  
 P<sub>CJ</sub> 378 kbar  
 m.p. 204°C  
 h<sub>50%</sub> 22-24 cm



TATB

Density 1.78 (1.93) g/cm<sup>3</sup>  
 VofD 7860 m/s  
 P<sub>CJ</sub> 277 kbar  
 m.p. 350°C  
 10/10 NF @ 200 cm

(The detonation parameters given above are those calculated using the empirical predictive formula of Rothstein and Petersen (Reference 2), while the densities are those calculated using the group additivity method of Holden (Reference 3); neither of which takes into consideration factors such as isomerism, molecular shape, and hydrogen bonding. The much higher measured density (in parenthesis) of TATB is a consequence of extensive intramolecular and intermolecular hydrogen bonding in that molecule, which is also responsible for its remarkable stability and insensitivity.)

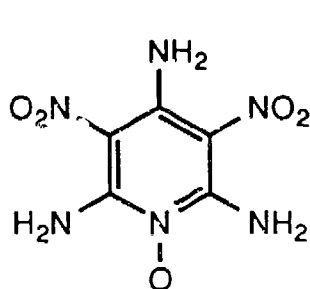
Such a material must also be tractable, allowing manipulation of crystalline morphology and size, and should be amenable to production at a viable cost. The very fact that such materials have not yet been developed attests that this is no trivial goal. The approach taken in this project is to start with the inherent stability associated with an aromatic azaheterocyclic ring system, and to combine this with the alternating nitro and amino groups which confer stability and insensitivity onto TATB and 1,3-diamino-2,4,6-trinitrobenzene (DATB). Where appropriate, the oxygen balance and, therefore presumably, the explosive performance are to be enhanced by the inclusion of the *N*-oxide functionality.

## RESULTS AND DISCUSSION

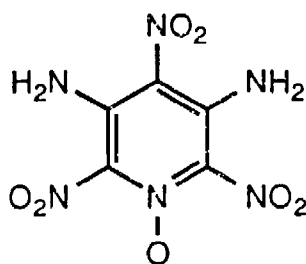
### POLYAMINOPOLYNITROPYRIDINE-1-OXIDES

Following this approach, two compounds which immediately come to mind are 2,4,6-triamino-3,5-dinitropyridine-1-oxide, and 3,5-diamino-2,4,6-trinitropyridine-1-oxide, whose predicted densities and detonation parameters

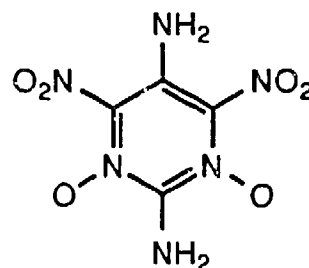
are given below. If the stability and insensitivity of these materials live up to expectations, then 2,5-diamino-4,6-dinitropyrimidine-1,3-dioxide might be considered, with predicted explosive properties which truly match those of RDX.



Density 1.81 g/cm<sup>3</sup>  
VofD 8010 m/s  
P<sub>CJ</sub> 291 kbar

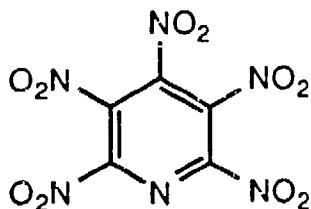


Density 1.90 g/cm<sup>3</sup>  
VofD 8650 m/s  
P<sub>CJ</sub> 351 kbar

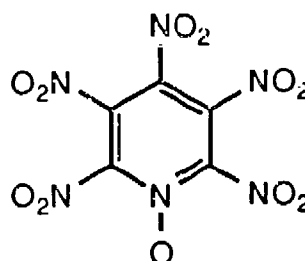


Density 1.92 g/cm<sup>3</sup>  
VofD 8930 m/s  
P<sub>CJ</sub> 377 kbar

(As an aside, it should also be noted that these materials may be potential synthons for the very energetic pentanitropyridine and its *N*-oxide, whose predicted parameters are also listed below.)



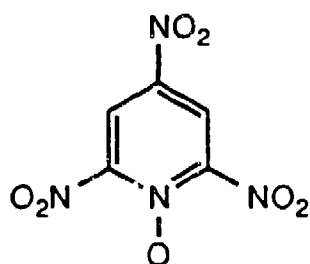
Density 1.95 g/cm<sup>3</sup>  
VofD 9290 m/s  
P<sub>CJ</sub> 411 kbar



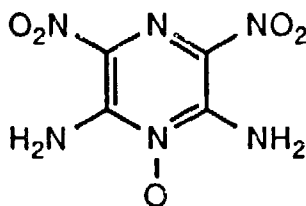
Density 2.07 g/cm<sup>3</sup>  
VofD 9050 m/s  
P<sub>CJ</sub> 388 kbar

There is some precedent for this type of explosive material. Ritter and Licht prepared 2,4,6-trinitropyridine-1-oxide (Reference 4), but found it to be like pentaerythritol tetranitrate (PETN) in its sensitivity. Pagoria prepared 2,6-diamino-3,5-dinitropyrazine-1-oxide (Reference 5), but found a drop height of 70 centimeters (cm). Coburn prepared 3,6-diamino-1,2,4,5-tetrazine-1,4-dioxide (LAX-112) (Reference 6) and found that it exceeds TATB and 3-nitro-1,2,4-triazole-5-one (NTO) in performance, but does not match RDX. The experimental densities are given in parentheses; note the higher than predicted densities (calculated from X-ray data) for the latter two compounds, attributed to hydrogen bonding between the amine functionalities and the adjacent *N*-oxide moieties.

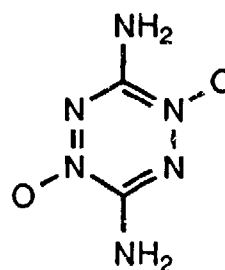




Density 1.86 (1.86) g/cm<sup>3</sup>  
 VolD 8370 m/s  
 PETN-like

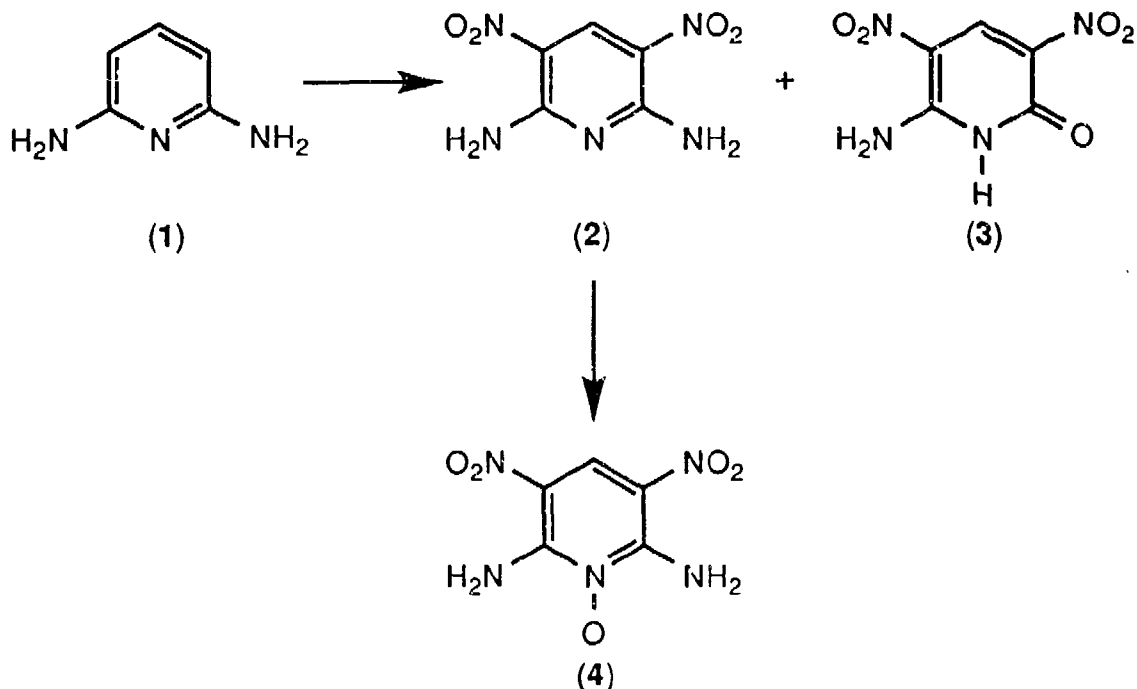


Density 1.84 (1.91) g/cm<sup>3</sup>  
 VolD 8730 m/s  
 h<sub>50%</sub> 70 cm



Density 1.81 (1.86) g/cm<sup>3</sup>  
 VolD 8780 m/s  
 h<sub>50%</sub> 179 cm

In a related program (Reference 7) it was shown that 2- and 4-aminopyridine could be nitrated in the 3- and/or 5-positions using mixtures of nitric and sulfuric acids. The reactions proceeded through a nitramine, which then underwent rearrangement to an aminonitropyridine, which could in turn be converted to the next nitramine and finally rearranged to 2- or 4-amino-3,5-dinitropyridine. The sequence could be carried out stepwise, with each intermediate being isolated in turn, or it could be performed as a concerted one-pot reaction without isolation of any of the intermediates. As an extension of this work, we found that 2,6-diaminopyridine (1) could also be nitrated using mixed nitric and sulfuric acids, first at 5°C and then at 65°C, to give 2,6-diamino-3,5-dinitropyridine (2). The product was always accompanied by 6-amino-3,5-dinitropyridone-2 (3), which is believed to be formed by hydrolysis of one of the presumed intermediate nitramines. The side-reaction can probably be avoided by using 100% nitric acid, but the contaminant may be removed as the sodium salt by extraction with boiling water. Oxidation of (2) with 30% hydrogen peroxide in acetic acid under reflux affords 2,6-diamino-3,5-dinitropyridine-1-oxide (4) in good yield.



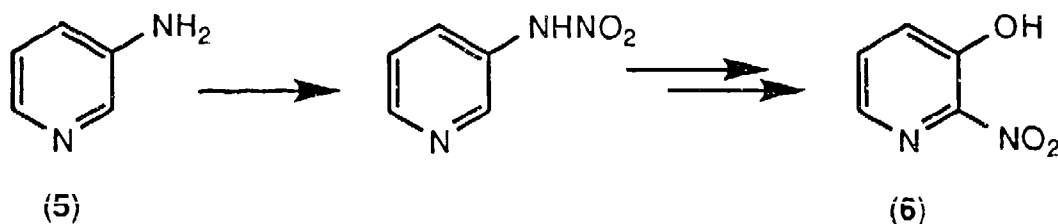
The *N*-oxide (4) was also prepared by Licht and Wanders (Reference 8), who noted its high melting point (greater than 340°C) and measured a density of 1.84 grams/cubic centimeter (g/cm<sup>3</sup>) by gas pycnometry and a drop weight impact sensitivity comparable with that of 2,4,6-trinitrotoluene (TNT). We found a density of 1.90 g/cm<sup>3</sup> (also by gas pycnometry), and were unable to initiate the material in a simple hammer/anvil screening test. These latter results were indicative of the extensive intramolecular hydrogen bonding sought in an insensitive energetic material. The predicted detonation velocity and pressure (7840 meters/second (m/s) and 275 kilobars (kbar)) do not match the performance desired and anticipated in the target compounds, but they do match those for TATB. Further, 4 may be recrystallized from several solvents (acetic acid, dioxane, dimethylformamide, *N*-methyl-2-pyrrolidinone), giving promise that the particle size and shape might be tailored more easily than TATB to meet a formulator's requirements. In addition, the cost of 2,6-diaminopyridine (1) is comparable with that of 1,3,5-trichlorobenzene from which TATB is prepared, indicating that manufacture of 4 may be a viable commercial possibility.

More recently, crystals suitable for X-ray analysis have been prepared by slow transfusion of dichloromethane into a solution of 4 in *N*-methyl-2-pyrrolidinone. Single crystal X-ray structure analysis was carried out at the Naval Research Laboratory (NRL), Washington, D.C., from which a crystal density of 1.878 g/cm<sup>3</sup> was determined, in excellent agreement with our gas pycnometry value. Further, the X-ray structure showed the expected extensive

hydrogen bonding, both intermolecular and intramolecular. The molecule is planar, with extended hydrogen bonding between the amine protons and both the adjacent nitro group and the *N*-oxide. The molecules are assembled head-to-tail in ribbons, the ribbons are assembled in sheets, and the sheets are stacked in a three dimensional array resembling that of TATB. However, the crystals are formed as flattened octahedra rather than as undesirable plates. The compound is insensitive to impact (10/10 no fires at 200 cm) and to friction (10/10 no fires at 100 pounds (lb)), and indistinguishable from TATB. There are some indications of slight electrostatic sensitivity, which can, however, be avoided by recrystallization. Initial formulation and performance characterization is currently in progress (Reference 7).

(Efforts have been made at the University of Maryland to predict the density of 2,6-diamino-3,5-dinitropyridine-1-oxide (4) using their density search program (Reference 9). Calculations based on the PM3 semi-empirical molecular orbital optimizations led to a predicted density of 1.841 g/cm<sup>3</sup>; calculations based on the molecular geometries optimized using the *ab initio* Gaussian 92 program (3-21g basis set), which better models strong hydrogen bonding, led to a predicted density of 1.860 g/cm<sup>3</sup>, within 1% of the value determined by X-ray crystallography.)

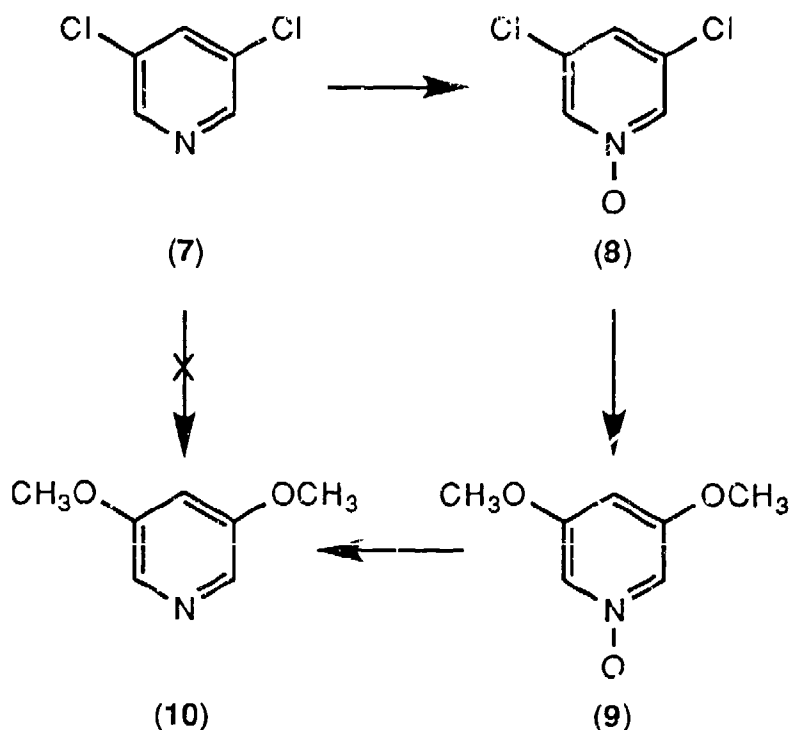
Nitration of 3-aminopyridine (5) did not proceed so smoothly; even under mild conditions the reaction "took off," and the product isolated was 3-hydroxy-2-nitropyridine (6). Presumably 6 was formed via facile acid hydrolysis of a 3-nitraminopyridine, and direct nitration of 3-aminopyridines does not appear to be a viable method for synthesis of 3,5-diamino-2,4,6-trinitropyridines.



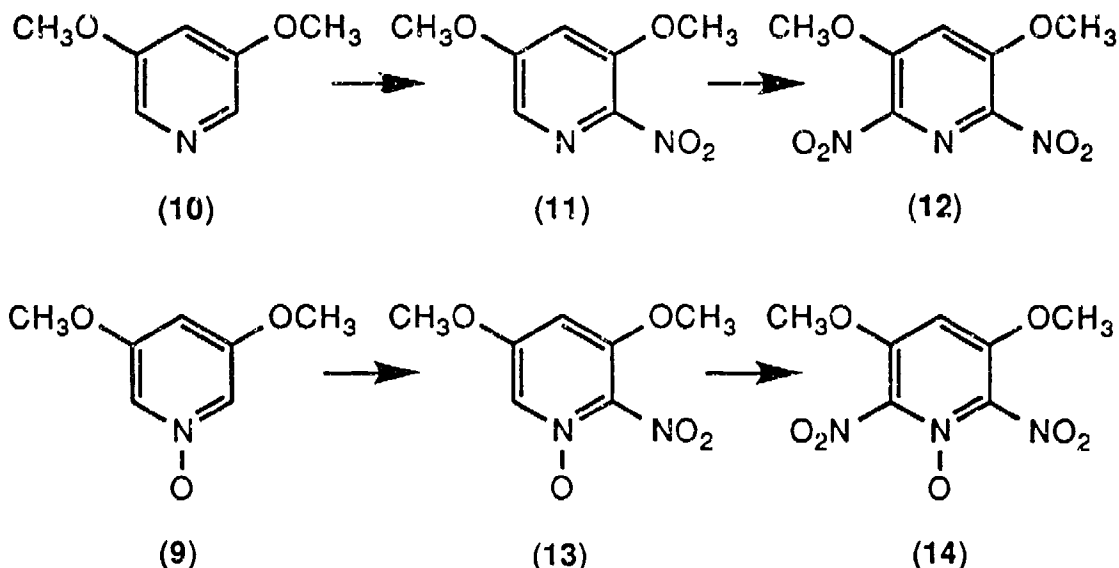
However, a review article by Katritzky (Reference 10) indicated that 3,5-dimethoxypyridine and its *N*-oxide could be nitrated in mixed acid, suggesting an alternative approach to 3,5-diamino-2,6-dinitropyridine-1-oxide, and also to 3,5-diamino-2,4,6-trinitropyridine-1-oxide, one of the target molecules. The former compound would be isomeric with 2,6-diamino-3,5-dinitropyridine-1-oxide (4) described above, but would not have the possibility of intramolecular hydrogen bonding between the amine protons and the *N*-oxide.

3,5-Dichloropyridine (7) may be transformed into the *N*-oxide (8) in a routine fashion (Reference 11), by treatment with 30% aqueous hydrogen

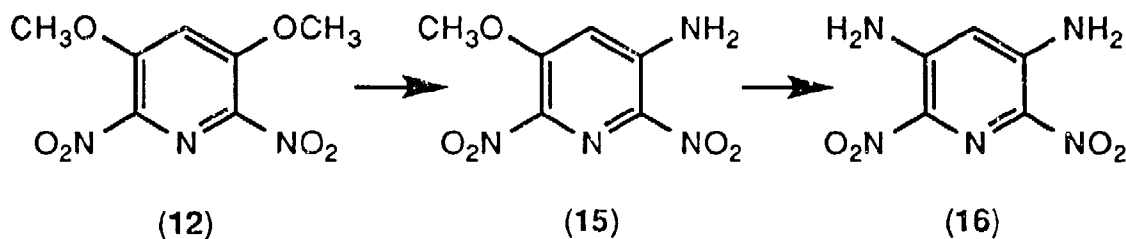
peroxide in acetic acid at 70°C, and thence to 3,5-dimethoxypyridine-1-oxide (9) by reaction with sodium methoxide in methanol under reflux (Reference 12). 3,5-Dimethoxypyridine (10) cannot be prepared directly from (7) under these conditions, but can be prepared by hydrogenation of (9) in ethanol using 5% palladium on charcoal as catalyst.

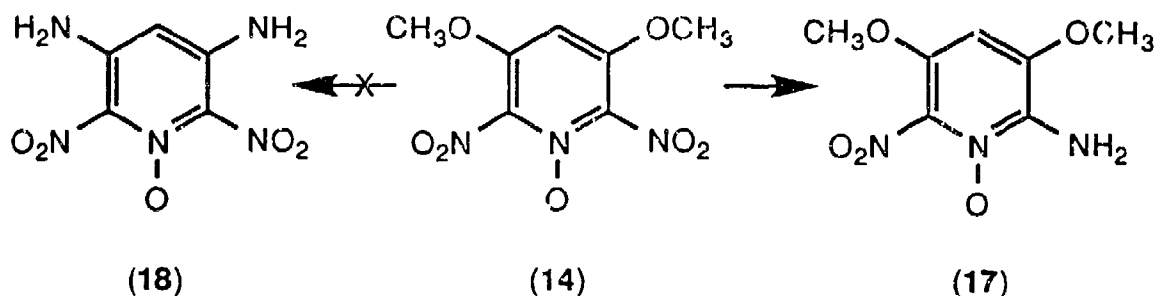


Nitration of 3,5-dimethoxypyridine (10) for 10 minutes (min) using a mixture of 96% sulfuric acid and 90% nitric acid at 0°C gave a 89% yield of 3,5-dimethoxy-2-nitropyridine (11); nitration of 10 for 22 hours (h) using a mixture of 96% sulfuric acid and 70% nitric acid at 40°C gave 3,5-dimethoxy-2,6-dinitropyridine (12) in 26% yield (Reference 12). Nitration of 3,5-dimethoxypyridine-1-oxide (9) for 2 h using a mixture of 96% sulfuric acid and 70% nitric acid at ambient temperature gave a 93% yield of 3,5-dimethoxy-2-nitropyridine-1-oxide (13); carrying out the reaction for 4 h at 90°C gave 3,5-dimethoxy-2,6-dinitropyridine-1-oxide (14) in 43% yield (Reference 13).

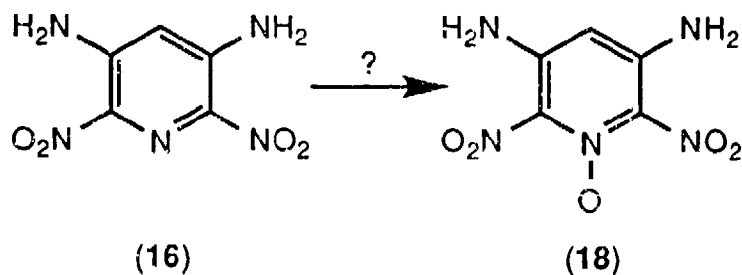


Ammonolysis of 3,5-dimethoxy-2,6-dinitropyridine (12) for 3 days using ethanolic ammonia under reflux gave 3-amino-5-methoxy-2,6-dinitropyridine (15) in quantitative yield. Further ammonolysis under more forcing conditions, using saturated ethanolic ammonia sealed in a Carius tube and heated for 5 days in an oven at 100°C, gave 3,5-diamino-2,6-dinitropyridine (16) isolated in 75% overall yield. However, ammonolysis of 3,5-dimethoxy-2,6-dinitropyridine-1-oxide (14) under a variety of conditions, from ambient temperature to 100°C, gave 2-amino-3,5-dimethoxy-6-nitropyridine-1-oxide (17), rather than the desired 3,5-diamino-2,6-dinitropyridine-1-oxide (18). Thus, stirring 14 in saturated ethanolic ammonia at ambient temperature for 1 week gave 17 in 78% yield. Clearly the *N*-oxide moiety is sufficiently electron-withdrawing that it activates the adjacent nitro group to nucleophilic displacement, and reaction takes place preferentially at the 2-position. This unexpected and undesired nucleophilic displacement of an aromatic nitro group has been observed in several previous studies (Reference 14).



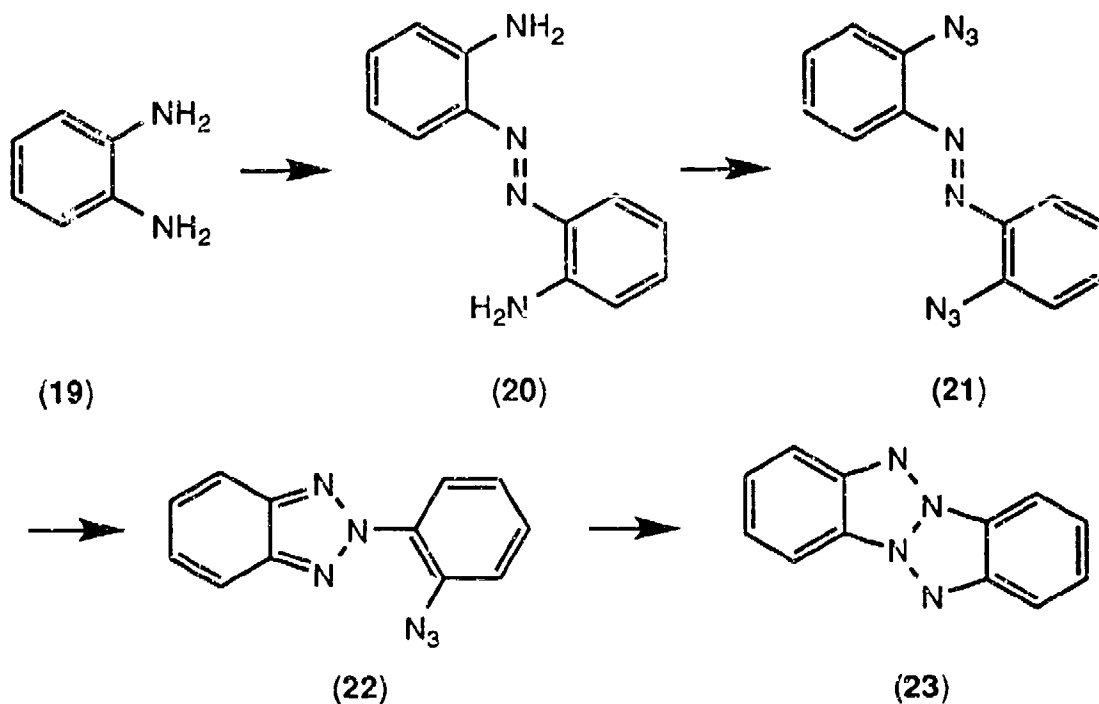


It seems reasonable that the *N*-oxide (18) should be accessible by oxidation of 3,5-diamino-2,6-dinitropyridine (16). However, 16 was recovered unchanged after being heated with 30% hydrogen peroxide in acetic acid under reflux, or after stirring with 30% hydrogen peroxide in trifluoroacetic acid at ambient temperature. Heating 16 with 30% hydrogen peroxide in trifluoroacetic acid under reflux simply resulted in decomposition. Alternative oxidizing agents will be evaluated for this conversion.

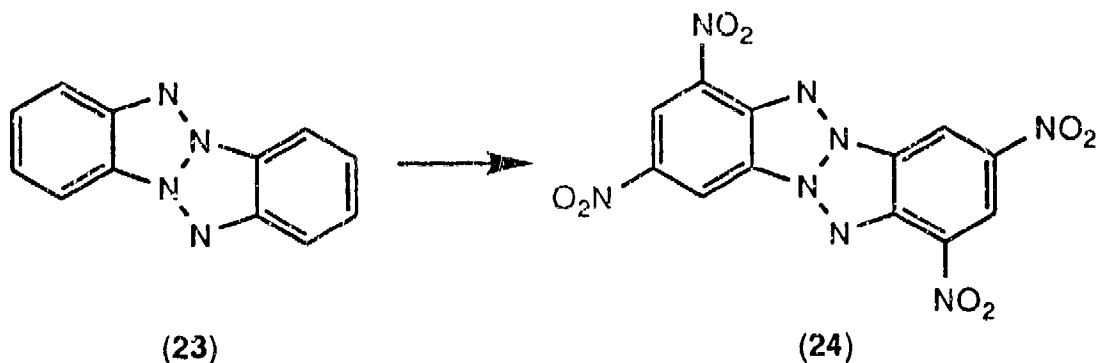


### DIBENZO-1,3a,4,6a-TETRAAZAPENTALENES

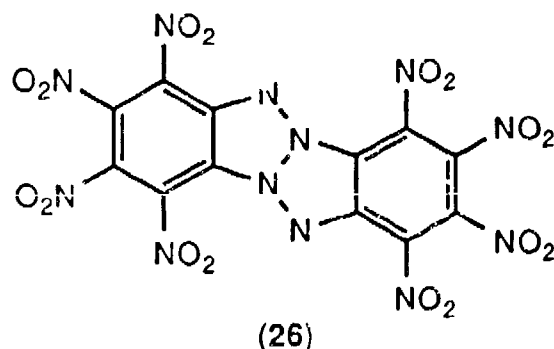
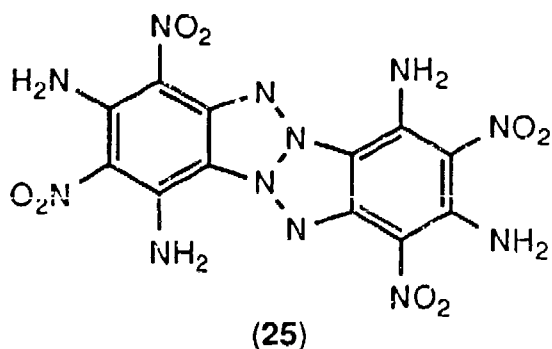
The parent dibenzo-1,3a,4,6a-tetraazapentalene (23) was prepared in good yield by thermolysis of 2,2'-diazidoazobenzene (21) (Reference 15). (23 has also been described as 5,11-dehydro-5H,11H-benzotriazolo[2,1-a]benzotriazole, but the trivial pentalene terminology is used here.) Treatment of *o*-phenylenediamine (19) with lead dioxide in benzene under reflux gave 2,2'-diaminoazobenzene (20), which was doubly diazotized and treated with excess sodium azide to give 21. Thermolysis of 21 in benzene under reflux afforded 2-(2'-azidophenyl)-2H-benzotriazole (22); thermolysis of 21 or 22 in decalin at 180°C resulted in smooth conversion to 23.



Diberzo-1,3a,4,6a-tetraazapentalene (23) has a high melting point (237-238°C), and is thermally very stable, being sublimable at atmospheric pressure without sign of decomposition. It is planar, and shows no detectable dipole moment or signs of isomerization, and as such seems an admirable skeletal system on which to base a thermally stable energetic material. Indeed, nitration of 23 easily afforded 2,4,8,10-tetranitrodibenzo-1,3a,4,6a-tetraazapentalene (24) in good yield (Reference 16). This is also a very stable material thermally, with a melting point of 410°C (dec), which also shows no sign of isomerization, particularly with the valence-isomeric 1,2,5,6-tetraazacyclooctatetraene structure; nonetheless, 24 has been endowed with the sobriquet TACOT.



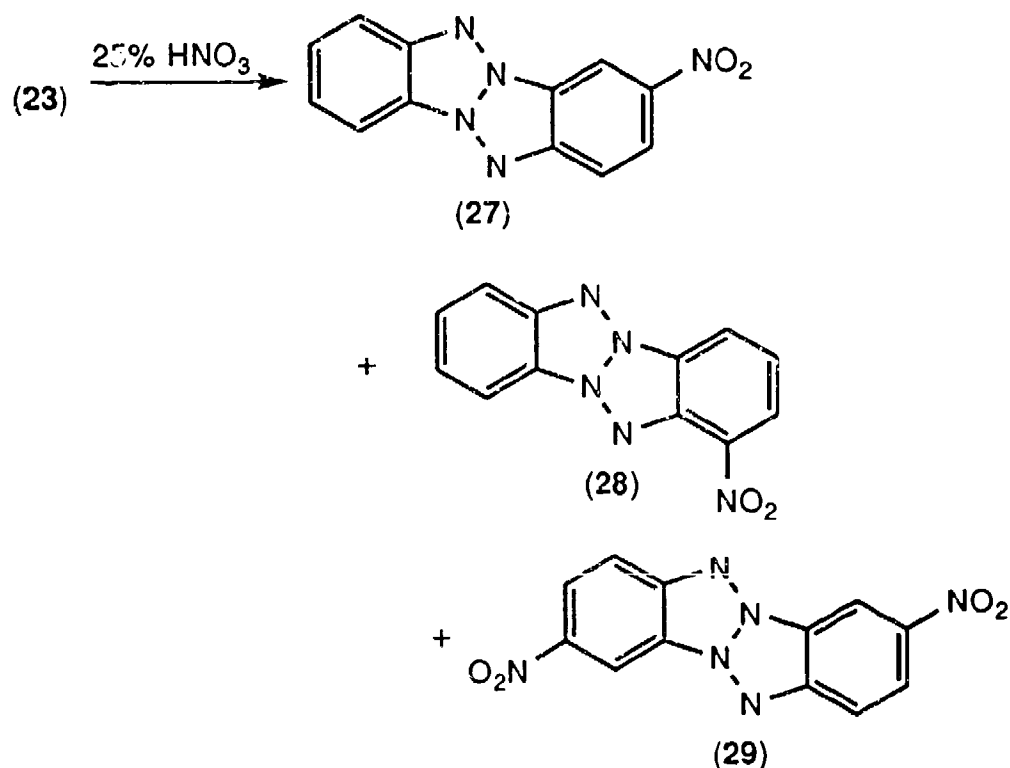
TACOT has a predicted density of  $1.82 \text{ g/cm}^3$ , matched by a measured crystal density of  $1.85 \text{ g/cm}^3$ . This property, coupled with its extraordinary thermal stability and insensitivity, has led to TACOT being used as a high temperature explosive, despite its rather unexceptional performance (velocity of detonation  $7060 \text{ m/s}$ , and detonation pressure  $203 \text{ kbar}$ ). The intention was, then, to augment the performance of TACOT by further substitution. Addition of four amino groups, as in tetraaminotetranitrodibenzotetraazapentalene (25), should increase both density ( $1.86 \text{ g/cm}^3$ ) and performance (velocity of detonation  $7570 \text{ m/s}$  and detonation pressure  $250 \text{ kbar}$ ) to some extent, while the alternating amino and nitro groups should ensure stability and insensitivity; inclusion of four additional nitro groups, as in octanitrodibenzotetraazapentalene (26), would markedly increase both density ( $2.00 \text{ g/cm}^3$ ) and performance (velocity of detonation  $8590 \text{ m/s}$  and detonation pressure  $346 \text{ kbar}$ ), but stability and insensitivity would be dependent on the inherent stability of the heterocyclic skeletal system.



Not unexpectedly, the presence of the nitro groups in TACOT (24) deactivates the compound to further electrophilic substitution, and, therefore, further nitro groups cannot be introduced by direct nitration. The original references indicated that nitration of the parent heterocycle (23) under much milder conditions should afford the mono- and dinitro derivatives (27) and (29) in good yield (Reference 16), and it was hoped to reduce these to the corresponding amines for further nitration. However, in our hands addition of (23) to 25% aqueous nitric acid at  $10^\circ\text{C}$  and warming to ambient temperature overnight gave a complex mixture.  $^1\text{H}$ -Nuclear magnetic resonance (NMR) indicated that this mixture was principally composed of 2-nitro isomer 27 (69%), but also contained the 4-nitro isomer 28 (27%), and the 2,8-dinitro compound 29 (3%), as well as unreacted heterocycle (23) and another dinitro derivative (probably the 2,10-isomer), both in trace amounts. The majority of 27 was separated by repeated washing with hot chloroform, and the remainder of 27 as well as 28, 29, and 23 were separated from the chloroform washings by repeated flash chromatography, using silica as adsorbent and chloroform as eluent. Each purified component was identified by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR, and by a battery of two-dimensional NMR experiments including Heteronuclear Multiple



Quantum Coherence (HMQC) short range and Heteronuclear Multiple Band Coherence (HMBC) long range proton-carbon coupling experiments and Totally Correlated Spectroscopy (TOCSY) proton total correlation experiments. The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR assignments are presented in Tables 1 and 2, respectively.



In a similar fashion, addition of **23** to 70% nitric acid and stirring below 0°C for 3 h gave a mixture of **29** (27%) and the 2,4,8-trinitro compound (**30**) (72%), as well as TACOT (**24**) (1%); again the components were separated using flash chromatography, and were identified by NMR methods. <sup>1</sup>H- and <sup>13</sup>C-NMR assignments are also given in Tables 1 and 2, respectively.

Moreover, catalytic hydrogenation of **27** and **29** did not occur smoothly, and this approach was, therefore, abandoned, at least temporarily.

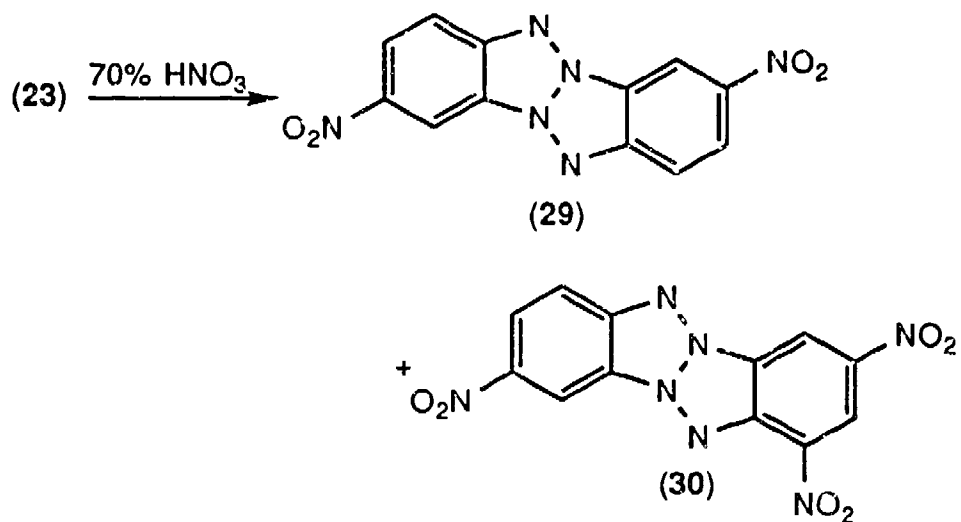


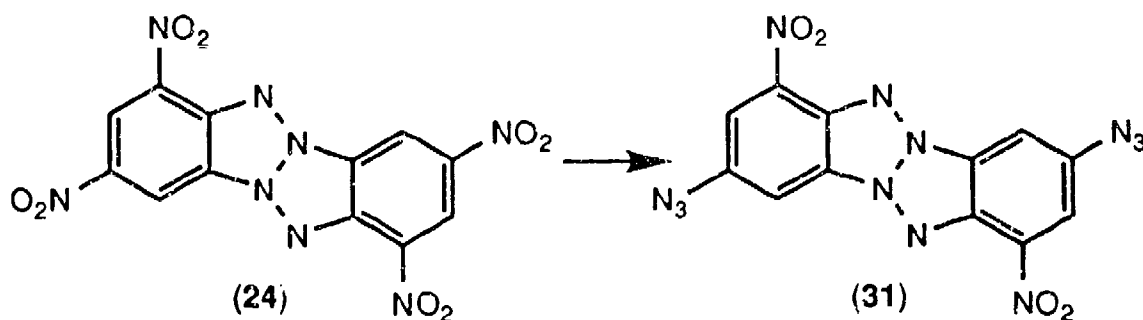
TABLE 1.  $^1\text{H-NMR}$  Chemical Shifts Of  
Dibenzo-1,3a,4,6a-tetraazapentalenes.

Chemical shift	23	27	28	29	30	24
H <sub>1</sub>	8.26	9.20	8.75	9.25	9.81	9.98
H <sub>2</sub>	7.45	...	7.54	...	...	...
H <sub>3</sub>	7.67	8.45	8.60	8.51	9.27	9.31
H <sub>4</sub>	7.97	8.08	...	8.26	...	...
H <sub>7</sub>	8.26	8.34	8.38	9.25	9.27	9.98
H <sub>8</sub>	7.45	7.62	7.59	...	...	...
H <sub>9</sub>	7.67	7.78	7.75	8.51	8.58	9.31
H <sub>10</sub>	7.97	8.14	8.08	8.26	8.43	...

TABLE 2.  $^{13}\text{C}$ -NMR Chemical Shifts of Dibenzo-1,3a,4,6a-tetraazapentalenes.

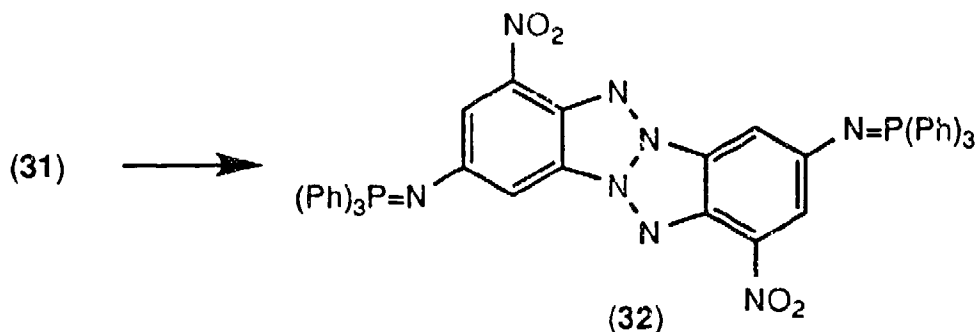
Chemical shift	23	27	28	29	30	24
C <sub>1a</sub>	117.23	116.63	120.71	117.00	120.53	121.15
C <sub>1</sub>	111.86	110.10	119.53	109.80	115.76	116.77
C <sub>2</sub>	121.91	140.19	119.49	141.98	140.72	141.28
C <sub>3</sub>	128.02	122.74	125.56	122.82	120.47	121.77
C <sub>4</sub>	116.56	116.50	134.02	117.59	133.48	134.49
C <sub>4a</sub>	145.81	148.20	139.03	147.79	139.39	140.89
C <sub>7a</sub>	117.23	118.27	118.15	117.00	118.79	121.15
C <sub>7</sub>	111.86	112.03	112.03	109.80	110.17	116.77
C <sub>8</sub>	121.91	124.42	124.12	141.98	143.68	141.28
C <sub>9</sub>	128.02	128.86	128.68	122.82	123.47	121.77
C <sub>10</sub>	116.56	117.59	117.33	117.59	118.79	134.49
C <sub>10a</sub>	145.81	145.99	146.03	147.79	147.96	140.89

Reaction of TACOT (24) with nucleophiles takes a somewhat unexpected course. Thus, treatment with lithium azide in hot dimethylformamide (DMF) resulted in displacement of nitro groups, and afforded a good yield of a diazido derivative, which was ascribed to the structure 31 (Reference 16). Lithium azide appears no longer to be available commercially, and simple substitution with sodium azide did not effect the desired displacement. This lack of reactivity is probably associated with insolubility of the sodium salt in DMF, and Professor Boyer (University of New Orleans) was able to modify this procedure by carrying the reaction out with sodium azide in dimethylsulfoxide (DMSO) to give 31 in moderate yield (Reference 17).

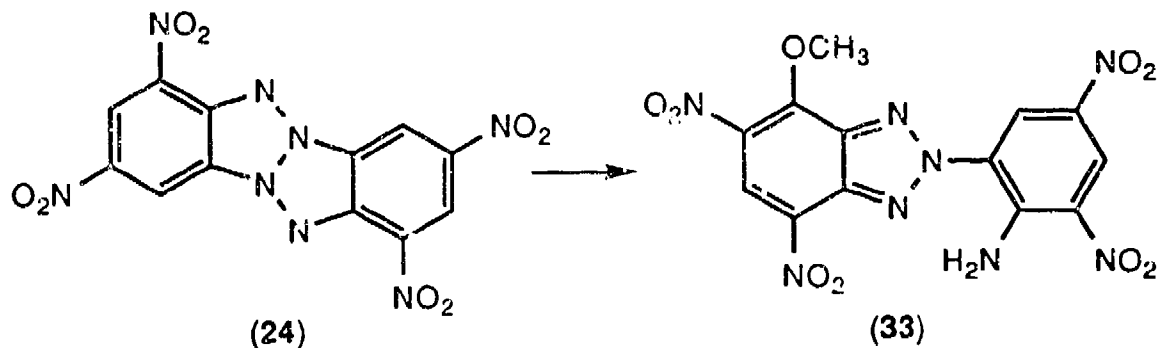


Treatment of 31 with triphenylphosphine in ethanol or benzene, at ambient temperature or under reflux, gave an essentially insoluble solid, which showed no sign of azide or azo grouping in the infrared spectrum, and the Staudinger-type structure (32) was tentatively assigned to this product

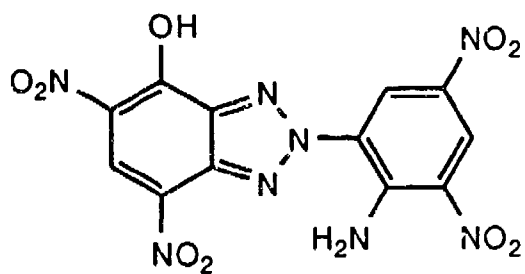
(Reference 18). However, attempted hydrolysis using hydrochloric acid and acetic acid, or using water in tetrahydrofuran, each at ambient temperature, gave no sign of the desired diamine. Alternative methods to achieve this hydrolysis will be pursued.



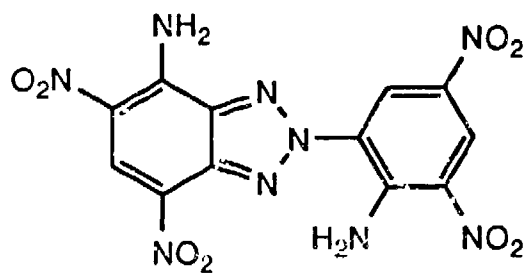
Our initial difficulties in repeating the synthesis of **31** prompted us to look further at the reaction of nucleophiles with TACOT (**24**), and the methoxide ion was selected because of the NMR "handle" it provides. Addition of TACOT to sodium methoxide in methanol at ambient temperature afforded an initial deep red solution; an orange solid precipitated, acidification of which yielded a yellow solid.  $^1\text{H-NMR}$  of a solution in  $\text{d}_6\text{-DMSO}$  showed an aromatic one proton singlet, an aromatic two proton AB signal, a broad amine signal and a single methoxyl signal; the infrared spectrum confirmed the presence of an amine functionality, suggesting cleavage of the tetraazapentalene ring system. HMQC short range and HMBC long range NMR coupling experiments were initially complicated by an unexpected instability of the material in DMSO, but more careful application of these techniques using freshly prepared solutions indicated the 2-phenylbenzotriazole structure **33** (or a positional isomer). Single crystal X-ray diffraction at the NRL confirmed the structure as **33**. These studies also showed the structure was (surprisingly) planar, with both intramolecular and intermolecular hydrogen bonding. This hydrogen bonding results in dimerization rather than extended planar sheets found in TATB or the corrugated sheets of TACOT, and may help stabilize the planar molecular conformation. Details of the structure determination are included in the appendix.



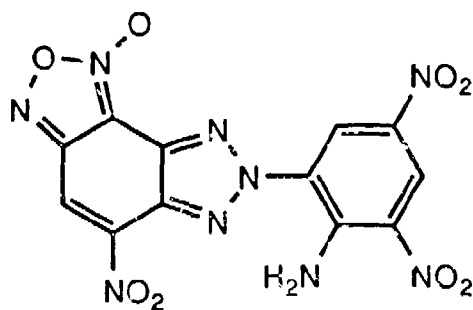
Solutions of **33** in  $d_6$ -DMSO decomposed or rearranged at ambient temperature with a half-life of 6-7 days. It is believed that **34** is probably the product, presumably derived by hydrolysis by residual water in the solvent. A solution of **33** in toluene was stable under reflux over the weekend; however, a solution of **33** in DMSO heated at  $80^\circ\text{C}$  overnight, quenched with water and extracted with dichloromethane gave a yellow solid whose  $^1\text{H}$ -NMR was almost identical with **34**. The aromatic region was indistinguishable and there was no methoxyl signal, but there were two moles of DMSO present, presumably as solvent of crystallization. The lability of the methoxyl group was further demonstrated by its displacement using ammonia in ethanol under reflux to give **35**. The methoxy compound (**33**) also reacted with azide ion in ethanol under reflux, yielding not the corresponding azido compound, but rather a ring fused furoxan derivative, believed to be **36**. The structures of **34**, **35**, and **36** were also assigned on the basis of  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra, which are presented in Tables 3 and 4, respectively, and on the basis of HMQC short range and HMBC long range coupling experiments.



(34)



(35)



(36)

TABLE 3. <sup>1</sup>H-NMR Chemical Shifts  
of 2-Phenylbenzotriazoles.

Chemical shift	3	34	35	36
H <sub>5</sub>	9.09	9.13	9.05	9.12
H <sub>4'</sub>	9.06	8.97	9.05	8.97
H <sub>6'</sub>	8.87	8.85	8.99	8.84
2'-NH <sub>2</sub>	8.45	8.81	8.90	8.81
Other	4.75 (OCH <sub>3</sub> )	...	9.50 (NH <sub>2</sub> )	...

TABLE 4.  $^{13}\text{C}$ -NMR Chemical Shifts  
for 2-Phenylbenzotriazoles.

Chemical shift	33	34	35	36
C <sub>3a</sub>	140.79	140.92	138.91	140.99
C <sub>4</sub>	132.80	130.36	125.61	130.34
C <sub>5</sub>	124.44	130.36	126.57	130.45
C <sub>6</sub>	128.71	117.36	122.85	164.62
C <sub>7</sub>	152.09	164.40	143.87	117.42
C <sub>7a</sub>	138.42	143.98	137.87	144.11
C <sub>1'</sub>	126.69	126.76	124.15	126.84
C <sub>2'</sub>	144.25	143.12	142.47	143.27
C <sub>3'</sub>	131.93	131.93	132.49	131.90
C <sub>4'</sub>	125.43	123.54	124.00	123.68
C <sub>5'</sub>	133.60	133.69	133.63	133.67
C <sub>6'</sub>	128.21	125.09	125.07	125.30
Other	63.68 (OCH <sub>3</sub> )	...	...	...

## CONCLUSIONS AND RECOMMENDATIONS

Advances have been made in understanding the chemistry of 2,6-dinitropyridines and their 1-oxides, and significant progress has been made towards the synthesis of 3,5-diamino-2,4,6-trinitropyridine-1-oxide, a compound expected to be a dense and energetic but insensitive explosive. The synthesis of 3,5-diamino-2,6-dinitropyridine has been achieved, and efforts will now be directed towards the further nitration and oxidation of this material.

The fascinating chemistry of the dibenzo-1,3a,4,6a-tetraazapentalene system has also been revisited. The application of flash column chromatography and sophisticated NMR techniques have revealed that the partial nitration of this material is more complex than previously believed. It is just as well that the complete nitration to TACOT is so facile and takes place in a convergent manner! It has also been shown that nucleophilic reactions involving TACOT are not necessarily straight forward, and can lead to cission of the tetraazapentalene ring system. It seems that the most profitable line for further derivatization of TACOT may well be vicarious amination, and this reaction will also be pursued, as will the synthesis of other pertinent nitro-substituted heterocyclic ring systems.

## EXPERIMENTAL SECTION

**WARNING:** Many of the compounds described in this report are potentially explosive, which may be subject to accidental initiation by such environmental stimuli as impact, friction, heat or electrostatic discharge. Therefore, appropriate precautions should be taken in their handling and/or use. Melting points were determined in capillary tubes using a Mel-Temp II melting point apparatus. Infrared (IR) spectra were determined in KBr disks using a Perkin-Elmer Model 1330 spectrophotometer.  $^1\text{H}$ -NMR spectra were determined in  $d_6$ -acetone or  $d_6$ -dimethylsulfoxide (DMSO) solutions, using an IBM NR-80 instrument at 80 megahertz (MHz) or a Bruker AMX-400 instrument at 400 MHz;  $^{13}\text{C}$ -NMR spectra were recorded on the latter instrument at 100 MHz, while the various two-dimensional NMR experiments were carried out on the same instrument. Mass spectra were determined using a Perkin-Elmer 5985 gas chromatograph/mass spectrometer (GC/MS).

**3,5-DICHLOROPYRIDINE-1-OXIDE (8)**

To a solution of 3,5-dichloropyridine (7) (27 g, 183 millimoles (mmol) in glacial acetic acid (150 milliliters (mL)) was added 30% aqueous hydrogen peroxide (25 mL), and the solution was heated at 70°C for 4 h. After standing at ambient temperature overnight, a further 25 mL of hydrogen peroxide was added, and the solution was again heated to 70°C for 4 h. As much acetic acid as possible was removed by distillation under vacuum, and water (100 mL) was added to the residue, which was then basified with potassium carbonate. Extraction with chloroform (3 x 100 mL) gave the *N*-oxide, which was recrystallized from heptane to give 8 as white needles (26.2 g, 88%), melting point (m.p.) 107-108°C (lit. 109°C (Reference 12)).  $^1\text{H}$ -NMR (acetone): 8.27 (d,  $J = 1.60$  Hz,  $\text{H}_{2,6}$ ), 7.54 (t,  $J = 1.60$  Hz,  $\text{H}_4$ ).

**3,5-DIMETHOXYPYRIDINE-1-OXIDE (9)**

3,5-Dichloropyridine-1-oxide (8) (24.9 g, 154 mmol) was added to methanolic sodium methoxide (30 g sodium in 250 mL methanol) and heated under reflux for 24 h. The methanol was removed under vacuum, and cold water (200 mL) was added, with cooling, to the residue. Extraction with chloroform (4 x 100 mL) gave a white residue (15 g, 64%). Recrystallization from ethyl acetate gave 9 as off-white needles (12 g, 51%), m.p. 91°C (lit. 91-93°C (Reference 12)).  $^1\text{H}$ -NMR (acetone): 7.58 (d,  $J = 2.01$  Hz,  $\text{H}_{2,6}$ ), 6.60 (t,  $J = 2.01$  Hz,  $\text{H}_4$ ), 3.86 (s,  $\text{OCH}_3$ ).



**3,5-DIMETHOXYPYRIDINE (10)**

3,5-Dimethoxypyridine-1-oxide (9) (7.0 g, 45 mmol) was dissolved in ethanol (120 mL) and hydrogenated over 5% palladium/charcoal (0.7 g) at ambient temperature overnight. Filtration and evaporation of the solvent gave **10** as a colorless oil (6.72 g, 93%). <sup>1</sup>H-NMR (acetone): 7.89 (d, J = 2.42 Hz, H<sub>2,6</sub>), 6.88 (t, J = 2.42 Hz, H<sub>4</sub>), 3.85 (s, OCH<sub>3</sub>).

**3,5-DIMETHOXY-2-NITROPYRIDINE (11)**

3,5-Dimethoxypyridine (10) (0.75 g, 5.4 mmol) was dissolved in 96% sulfuric acid (15 mL) and cooled to 0°C. Mixed acid (90% nitric acid (0.5 mL) in 96% sulfuric acid (10 mL)) was added dropwise at 0°C, and the reaction mixture was held at that temperature for 10 min. Quenching on ice, filtration, and washing with cold water gave a yellow solid (0.88 g, 89%), recrystallized from aqueous ethanol to give **11** as yellow crystals, m.p. 113.5-115.5°C (lit. 117-118.5°C (Reference 12)). IR: 1600, 1570, 1520, 1430, 1410, 1360, 1330, 1260, 1240, 1210, 1110, 1000, 860, 840, 700 cm<sup>-1</sup>. <sup>1</sup>H-NMR (acetone): 7.73 (d, J = 2.35 Hz, H<sub>6</sub>), 7.37 (d, J = 2.35 Hz, H<sub>4</sub>), 4.02 (s, OCH<sub>3</sub>). <sup>13</sup>C-NMR (acetone): 161.14 (C<sub>5</sub>), 150.36 (C<sub>3</sub>), 143.4 (C<sub>2</sub>), 126.74 (C<sub>6</sub>), 108.68 (C<sub>4</sub>), 57.26 (OCH<sub>3</sub>), 57.16 (OCH<sub>3</sub>). M/z: 184 (parent ion), 154, 138, 108 (base peak), 93, 78.

**3,5-DIMETHOXY-2,6-DINITROPYRIDINE (12)**

3,5-Dimethoxypyridine (10) (1.5 g, 10.8 mmol) was dissolved in 96% sulfuric acid (50 mL) and 70% nitric acid (10 mL) was added dropwise and with stirring at ambient temperature. The solution was heated to 40°C for 22 h, quenched on ice, and the precipitate filtered and washed with cold water to give a yellow powder (0.65 g, 36%). Recrystallization from ethanol gave **12** as very pale yellow needles (0.55 g, 22%), m.p. 178-180°C (lit. 181-182°C (Reference 12)). IR: 1600, 1580, 1480, 1460, 1430, 1380, 1320, 1290, 1230, 1150, 1100, 1000, 870, 860, 840, 710, 690 cm<sup>-1</sup>. <sup>1</sup>H-NMR (acetone): 7.86 (s, H<sub>4</sub>), 4.21 (s, OCH<sub>3</sub>). <sup>13</sup>C-NMR (acetone): 154.32 (C<sub>3,5</sub>), 137.25 (C<sub>2,6</sub>), 111.35 (C<sub>4</sub>), 58.70 (OCH<sub>3</sub>). M/z: 229 (parent ion), 213, 199, 183, 169, 153, 111, 107 (base peak).

**3,5-DIMETHOXY-2-NITROPYRIDINE-1-OXIDE (13)**

3,5-Dimethoxypyridine-1-oxide (9) (1.25 g, 8.1 mmol) was dissolved in 96% sulfuric acid (25 mL) at 0°C, and 70% nitric acid (0.5 mL) was added dropwise at that temperature. The solution was allowed to warm to ambient temperature, and after 2 h was quenched in ice/water (250 mL). Neutralization with potassium carbonate and extraction with chloroform (4 x 100 mL) gave a

pale yellow crystalline solid (1.5 g, 93%). Recrystallization from ethanol gave **13** as yellow plates (1.4 g, 87%), m.p. 174-175.5°C (lit. 168-169°C (Reference 13)). IR: 3080, 1600, 1570, 1540, 1480, 1440, 1400, 1380, 1350, 1230, 1200, 1170, 1160, 1130, 1030, 980, 850, 830, 810, 650  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (acetone): 7.77 (d,  $J = 2.12$  Hz,  $\text{H}_6$ ), 7.01 (d,  $J = 2.12$  Hz,  $\text{H}_4$ ), 4.04 (s,  $\text{OCH}_3$ ), 3.98 (s,  $\text{OCH}_3$ ).  $^{13}\text{C-NMR}$  (acetone): 159.36 ( $\text{C}_5$ ), 150.64 ( $\text{C}_3$ ), 141.37 ( $\text{C}_2$ ), 121.22 ( $\text{C}_6$ ), 99.80 ( $\text{C}_4$ ), 58.17 ( $\text{OCH}_3$ ), 57.62 ( $\text{OCH}_3$ ).  $\text{M/z}$ : 200 (parent ion), 170, 140, 125, 108, 69 (base peak).

### 3,5-DIMETHOXY-2,6-DINITROPYRIDINE-1-OXIDE (**14**)

3,5-Dimethoxypyridine-1-oxide (**9**) (1.0 g, 6.5 mmol) was dissolved in 96% sulfuric acid at ambient temperature, and 70% nitric acid (1.5 mL) was added dropwise and with stirring. The solution was warmed to 90°C and maintained at that temperature for 4 h. Quenching in ice/water (250 mL) and filtration gave a pale yellow/off-white solid (0.66 g, 42%). Recrystallization from ethanol/acetone gave **14** as a pale yellow solid (0.36 g, 23%), m.p. 265-267°C (dec) (lit. 260-261°C (Reference 13)). IR: 3090, 1580, 1550, 1480, 1440, 1410, 1360, 1220, 1200, 1130, 970, 830, 820, 690  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (acetone): 7.55 (s,  $\text{H}_4$ ), 4.19 (s,  $\text{OCH}_3$ ).  $^{13}\text{C-NMR}$  (acetone): 151.59 ( $\text{C}_{3,5}$ ), 139.72 ( $\text{C}_{2,6}$ ), 99.65 ( $\text{C}_4$ ), 59.16 ( $\text{OCH}_3$ ).  $\text{M/z}$ : 245 (parent ion), 215, 185, 169, 153, 127, 126, 110 (base peak).

### 3-AMINO-5-METHOXY-2,6-DINITROPYRIDINE (**15**)

3,5-Dimethoxy-2,6-dinitropyridine (**12**) (0.35 g, 1.5 mmol) was added to ethanol (100 mL), and the mixture was saturated with ammonia gas and heated under reflux for 20 h. Evaporation to dryness gave a bright yellow solid (0.32 g, 99%), which was recrystallized from ethanol to give **15** as yellow needles (0.22 g, 69%), m.p. 140-150°C (dec). IR: 3460, 3320, 1640, 1600, 1560, 1530, 1420, 1260, 1100  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (acetone): 7.55 (br s,  $\text{NH}_2$ ), 7.35 (s,  $\text{H}_4$ ), 4.04 (s,  $\text{OCH}_3$ ).  $^{13}\text{C-NMR}$  (acetone): 154.10 ( $\text{C}_5$ ), 146.93 ( $\text{C}_3$ ), 135.99 ( $\text{C}_6$ ), 130.14 ( $\text{C}_2$ ), 111.11 ( $\text{C}_4$ ), 57.83 ( $\text{OCH}_3$ ).  $\text{M/z}$ : 214 (parent ion), 184, 168, 154, 138, 137, 109, 95 (base peak).

### 3,5-DIAMINO-2,6-DINITROPYRIDINE (**16**)

(a) 3-Amino-2,6-dinitro-5-methoxypyridine (**15**) (0.25 g, 1.2 mmol) was added to ethanol (20 mL) in a Carius tube, and ammonia gas was bubbled in until saturation. The tube was sealed and then heated in an oven at 100°C over the weekend. Filtration yielded brown needles, recrystallized from N-methylpyrrolidinone/dichloromethane as **16** (0.15 g, 65%), m.p. >350°C (chars from

300°C). IR: 3480, 3380, 3340, 1660, 1560, 1490, 1320, 1240, 890  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (DMSO): 7.53 (br s,  $\text{NH}_2$ ), 6.70 (s,  $\text{H}_4$ ).  $^{13}\text{C-NMR}$  (DMSO): 145.02 ( $\text{C}_{3,5}$ ), 129.39 ( $\text{C}_{2,6}$ ), 108.18 ( $\text{C}_4$ ).

(b) 3,5-Dimethoxy-2,6-dinitropyridine (12) (1.15 g, 5.5 mmol) was added to ethanol (100 mL), and the solvent saturated with ammonia gas. The mixture was heated under reflux for 3 days, and the solvent was removed under vacuum;  $^1\text{H-NMR}$  indicated 95% conversion to 15. The residue was placed in a Carius tube with ethanol (25 mL) saturated with ammonia, and the tube was sealed and heated in an oven at 100°C for a week. The solid was filtered off to give 16 as a brown solid (0.75 g, 75%).

## 2-AMINO-3,5-DIMETHOXY-6-NITROPYRIDINE-1-OXIDE (17)

3,5-Dimethoxy-2,6-dinitropyridine-1-oxide (14) (0.35 g, 1.4 mmol) was added to ethanol (50 mL), and ammonia gas was bubbled in until saturation. The flask was sealed, and the reaction mixture was stirred at ambient temperature for 2 weeks. Filtration gave an orange powder (0.24 g, 78%). Recrystallization from ethanol gave 17 as orange crystals, m.p. 177-179°C. IR: 3440, 3220, 3180, 1600, 1580, 1550, 1530, 1230, 1180, 1130, 1080, 820  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (DMSO): 7.19 (s,  $\text{H}_4$ ), 6.10 (br s,  $\text{NH}_2$ ), 3.94 (s,  $\text{OCH}_3$ ), 3.87 (s,  $\text{OCH}_3$ ).  $^{13}\text{C-NMR}$  (DMSO): 147.01 ( $\text{C}_3$ ), 143.13 ( $\text{C}_2$ ), 141.84 ( $\text{C}_5$ ), 137.13 ( $\text{C}_6$ ), 106.42 ( $\text{C}_4$ ), 57.85, ( $\text{OCH}_3$ ), 56.63, ( $\text{OCH}_3$ ).  $\text{M/z}$ : 215 (parent ion), 198, 168, 151, 137, 123, 110 (base peak), 69. The same product was obtained if the reaction was carried out under reflux, or in a Carius tube at 100°C.

## DIBENZO-1,3a,4,6a-TETRAAZAPENTALENE (23)

Lead dioxide (23.9 g, 100 mmol) was added to a stirred mixture of *o*-phenylenediamine (19) (4.5 g, 41.7 mmol) in benzene (200 mL) at ambient temperature. The reaction mixture was stirred at ambient temperature for 1 h, and was then heated under reflux (with stirring) for 3 h. The insoluble lead salts were removed by filtration and the solution was cooled. Thirty-seven percent hydrochloric acid (15 mL) was added, and the precipitate was filtered off. Suspension in water (40 mL) and basification to pH 9 with solid sodium hydroxide gave a deeply colored solution, which was extracted with dichloromethane (4 x 150 mL). Recrystallization of the extract twice from benzene gave 2,2'-diaminoazobenzene (20) (1.5 g, 34%). 2,2'-Diaminoazobenzene (20) (5.4 g, 25.4 mmol) was added to a mixture of 37% hydrochloric acid (40 mL) and water (50 mL) and cooled to 0-2°C with stirring. A solution of sodium nitrite (4.4 g) in water (25 mL) was added dropwise and with stirring, maintaining the temperature below 10°C. Stirring was continued for 1 h, and sodium azide (4.0 g) in water (25 mL) was added at 5°C with stirring. Nitrogen

was evolved and a precipitate was formed. Stirring was continued for 2 h, and the solid was filtered off and dried to give 2,2'-diazidoazobenzene (**21**) (2.60 g, 39%). 2,2'-Diazidoazobenzene (**21**) (2.6 g, 10 mmol) was dissolved in benzene (200 mL) and heated under reflux for 2 h. The solution was decolorized with charcoal and evaporated to dryness to leave a waxy solid identified as 2-(2-azidophenyl)-benzotriazole (**22**) (2.07 g, 89%). 2-(2-Azidophenyl)-benzotriazole (**22**) (2.07 g, 8.8 mmol) was added to decalin (50 mL) and heated to 185°C with stirring for 2 h. The solution was decolorized with charcoal and allowed to cool, and the pale tan solid was filtered off to give dibenzo-1,3a,4,6a-tetraazapentalene (**23**) (1.43 g, 78%), m.p. 220-224°C (dec) (lit. 237-238°C (Reference 15)). IR: 1610, 1485, 1435, 1380, 1330, 1250, 1155, 1140, 1100, 810, 750, 730, 630  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (DMSO): 8.26 (ddd,  $J = 8.44, 1.00, 0.82$  Hz,  $\text{H}_{1,7}$ ), 7.97 (ddd,  $J = 8.68, 0.82, 0.82$  Hz,  $\text{H}_{4,10}$ ), 7.67 (ddd,  $J = 8.68, 6.96, 1.00$  Hz,  $\text{H}_{3,9}$ ), 7.45 (ddd,  $J = 8.44, 6.96, 0.82$  Hz,  $\text{H}_{2,8}$ ).  $^{13}\text{C-NMR}$  (DMSO): 145.81 ( $\text{C}_{4a,10a}$ ), 128.02 ( $\text{C}_{3,9}$ ), 121.91 ( $\text{C}_{2,8}$ ), 117.23 ( $\text{C}_{1a,7a}$ ), 116.56 ( $\text{C}_{4,10}$ ), 111.86 ( $\text{C}_{1,7}$ ).

#### NITRATION OF DIBENZO-1,3a,4,6a-TETRAAZAPENTALENE (**23**)

(a) Dibenzo-1,3a,4,6a-tetraazapentalene (**23**) (1.25 g, 6.0 mmol) was added to 25% nitric acid (17.5 mL) with stirring at 10°C, and the suspension was allowed to warm slowly to ambient temperature over about 2 h. The reaction mixture was stirred at ambient temperature over night to give an orange solid (1.40 g), which was filtered off and washed with water. Washing with chloroform (50 mL) over the weekend left an orange/yellow solid (1.07 g, 70%), which was recrystallized from chloroform to give **27**, m.p. 295-297°C (lit. 301-303°C (Reference 16)).  $^1\text{H-NMR}$  (DMSO): 9.20 (d,  $J = 2.24$  Hz,  $\text{H}_1$ ), 8.45 (dd,  $J = 9.44, 2.24$  Hz,  $\text{H}_3$ ), 8.34 (dd,  $J = 7.68, 0.91$  Hz,  $\text{H}_7$ ), 8.14 (dd,  $J = 8.76, 0.84$  Hz,  $\text{H}_{10}$ ), 8.08 (d,  $J = 9.44$  Hz,  $\text{H}_4$ ), 7.78 (ddd,  $J = 8.76, 7.44, 0.91$  Hz,  $\text{H}_9$ ), 7.62 (ddd,  $J = 7.68, 7.44, 0.84$  Hz,  $\text{H}_8$ ).  $^{13}\text{C-NMR}$  (DMSO): 148.20 ( $\text{C}_{4a}$ ), 145.99 ( $\text{C}_{10a}$ ), 140.19 ( $\text{C}_2$ ), 128.86 ( $\text{C}_9$ ), 124.42 ( $\text{C}_8$ ), 122.74 ( $\text{C}_3$ ), 118.27 ( $\text{C}_{7a}$ ), 117.59 ( $\text{C}_{10}$ ), 116.63 ( $\text{C}_{1a}$ ), 116.50 ( $\text{C}_4$ ), 112.03 ( $\text{C}_7$ ), 110.10 ( $\text{C}_1$ ). The chloroform washings were separated by repeated flash column chromatography (silica/chloroform) to give unreacted **23** (0.025 g), additional **27** (0.12 g, 8%), **28** (0.12 g, 8%), and **29** (0.04 g, 2%). Recrystallization of **28** from chloroform/heptane gave red/orange crystals, m.p. 255-258°C (dec). IR: 1615, 1525, 1510, 1480, 1380, 1360, 1330, 1280, 1260, 1130, 1090, 890, 810, 750, 735  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (DMSO): 8.75 (dd,  $J = 8.12, 0.90$  Hz,  $\text{H}_1$ ), 8.60 (dd,  $J = 8.08, 0.90$  Hz,  $\text{H}_3$ ), 8.38 (dd,  $J = 8.48, 0.96$  Hz,  $\text{H}_7$ ), 8.08 (dd,  $J = 8.72, 0.80$  Hz,  $\text{H}_{10}$ ), 7.75 (ddd,  $J = 8.72, 7.00, 0.96$  Hz,  $\text{H}_9$ ), 7.59 (ddd,  $J = 8.48, 7.00, 0.80$  Hz,  $\text{H}_8$ ), 7.54 (dd,  $J = 8.12, 8.08$  Hz,  $\text{H}_2$ ).  $^{13}\text{C-NMR}$  (DMSO): 146.03 ( $\text{C}_{10a}$ ), 139.03 ( $\text{C}_{4a}$ ), 134.02 ( $\text{C}_4$ ), 128.68 ( $\text{C}_9$ ), 125.56 ( $\text{C}_3$ ), 124.12 ( $\text{C}_8$ ), 120.71 ( $\text{C}_{1a}$ ), 119.53 ( $\text{C}_1$ ), 119.49 ( $\text{C}_2$ ), 118.15 ( $\text{C}_{7a}$ ), 117.33 ( $\text{C}_{10}$ ), 112.03 ( $\text{C}_7$ ).

(b) Dibenzo-1,3a,4,6a-tetraazapentalene (**23**) (0.10 g, 0.48 mmol) was added in small portions to 70% nitric acid (3 mL) at ice/salt bath temperatures, and stirred for about 3 h; the temperature did not exceed 0°C. The mixture was quenched in ice/water (100 mL), to give an orange/yellow solid (0.14 g) identified by <sup>1</sup>H-NMR as a mixture of two major components. Separation by repeated flash column chromatography (silica/chloroform), afforded **29** (0.04 g, 28%), **30** (0.10 g, 60%), and a trace of TACOT (**24**). Recrystallization gave **29** as a yellow solid, m.p. 333-338°C (dec) (lit. 340°C (dec) (Reference 16)). IR: 1610, 1590, 1520, 1355, 1330, 1290, 1110, 850, 830, 750, 725, 710 cm<sup>-1</sup>. <sup>1</sup>H-NMR (DMSO): 9.25 (d, J = 2.16 Hz, H<sub>1,7</sub>), 8.51 (dd, J = 9.48, 2.16 Hz, H<sub>3,9</sub>), 8.26 (d, J = 9.48, H<sub>4,10</sub>). <sup>13</sup>C-NMR: 147.79 (C<sub>4a,10a</sub>), 141.98 (C<sub>2,8</sub>), 122.82 (C<sub>3,9</sub>), 117.59 (C<sub>4,10</sub>), 117.00 (C<sub>1a,7a</sub>), 109.80 (C<sub>1,7</sub>). Recrystallization of **30** from chloroform gave an orange solid, m.p. 270-271°C. IR: 1620, 1600, 1540, 1520, 1420, 1355, 1330, 1300, 1290, 1160, 1110, 900, 820, 750, 740, 730, 710 cm<sup>-1</sup>. <sup>1</sup>H-NMR (DMSO): 9.81 (d, J = 2.08 Hz, H<sub>1</sub>), 9.48 (d, J = 2.16 Hz, H<sub>7</sub>), 9.27 (d, J = 2.08 Hz, H<sub>3</sub>), 8.58 (dd, 9.48, 2.16 Hz, H<sub>9</sub>), 8.43 (d, J = 9.48 Hz, H<sub>10</sub>). <sup>13</sup>C-NMR (DMSO): 147.96 (C<sub>10a</sub>), 143.68 (C<sub>8</sub>), 140.72 (C<sub>2</sub>), 139.39 (C<sub>4a</sub>), 133.48 (C<sub>4</sub>), 123.47 (C<sub>9</sub>), 120.87 (C<sub>3</sub>), 120.53 (C<sub>1a</sub>), 118.79 (C<sub>10</sub>), 118.05 (C<sub>7a</sub>), 115.76 (C<sub>1</sub>), 110.17 (C<sub>7</sub>). TACOT (**24**) is an orange/red powder, m.p. >380°C (lit. 410 (dec) (Reference 16)). IR: 3100, 1620, 1530, 1480, 1410, 1355, 1325, 1280, 1135, 1070, 1050, 820, 745 cm<sup>-1</sup>. <sup>1</sup>H-NMR (DMSO): 9.98 (d, J = 2.02 Hz, H<sub>1,7</sub>), 9.31 (d, J = 2.02 Hz, H<sub>3,9</sub>). <sup>13</sup>C-NMR (DMSO): 141.28 (C<sub>2,8</sub>), 140.89 (C<sub>4a,10a</sub>), 134.49 (C<sub>4,10</sub>), 121.77 (C<sub>3,9</sub>), 121.15 (C<sub>1a,7a</sub>), 116.77 (C<sub>1,7</sub>).

## **2,8-DIAZIDO-4,10-DINITRODIBENZO-1,3a,4,6a-TETRAAZAPENTALENE (**31**) (Reference 17)**

2,4,8,10-Tetranitro-1,3a,4,6a-tetraazapentalene (TACOT, **24**) (1.55 g, 4.0 mmol) was added to DMSO (33.5 mL) and stirred at ambient temperature. Sodium azide was added slowly with stirring at ambient temperature, and after 15 min the mixture was warmed to 70°C and held at that temperature for 1 h, turning very deep red in color. The mixture was cooled to 15°C in ice/water, and the orange solid was filtered off and washed with ethanol (5 mL) and finally ether (5 mL) to give **31** (0.60 g, 41%), m.p. 197°C (dec) (lit. 200°C (dec) (Reference 16)). IR: 2120, 1600, 1525, 1360, 1330, 1290, 1135, 960, 880, 810, 740 cm<sup>-1</sup>.

**2,8-BIS(TRIPHENYLPHOSPHINIMINO)-  
4,10-DINITRODIBENZO-1,3a,4,6a-  
TETRAAZAPENTALENE (32)**

2,8-Diazido-4,10-dinitrodibenzo-1,3a,4,6a-tetraazapentalene (31) (0.10 g, 0.26 mmol) and triphenylphosphine (0.15 g, 0.57 mmol) were stirred in benzene (50 mL) for 24 h, forming a purple solution and a dark purple solid. Filtration gave a purple solid (0.15 g), m.p. >350°C (chars from 300°C). When the reaction was carried out in ethanol at ambient temperature for 24 h or in benzene solution under reflux for 4 h, the same product was obtained (0.19 g and 0.20 g, respectively). This material was too insoluble for measurement of NMR spectra, but the IR spectra displayed clean, sharp signals, with a notable absence of any azide signals around 2100  $\text{cm}^{-1}$ . The compound was tentatively identified with the structure 32. IR: 1600, 1515, 1495, 1440, 1355, 1335, 1370, 1110, 1090, 730, 700, 530  $\text{cm}^{-1}$ .

**2-(2'-AMINO-3',5'-DINITROPHENYL)-7-METHOXY-  
4,6-DINITROBENZOTRIAZOLE (33)**

2,4,8,10-Tetranitrodibenzo-1,3a,4,6a-tetraazapentalene (TACOT, 24) (1.00 g, 3.6 mmol) was added to methanolic sodium methoxide (1.00 g sodium metal in 100 mL methanol) at ambient temperature. The solid appeared to dissolve to give a deep red solution, whereupon an orange solid started to appear. After stirring the reaction mixture at ambient temperature for 24 h, the solid was filtered off and washed with a little cold methanol (10 mL) to give a dirty orange solid. Suspension in methanol (100 mL) and stirring at ambient temperature for 3 h gave a clean orange solid (1.13 g), probably a Meisenheimer salt. ( $^1\text{H-NMR}$  (DMSO): 9.04 (br s,  $-\text{NH}_2$ ), 9.02 (s, 1H), 8.90 (d,  $J = 2.76$  Hz, 1H), 8.80 (d,  $J = 2.76$  Hz, 1H), 3.07 (s,  $-\text{OCH}_3$ , 6H).) Suspension in water (100 mL) and acidification with 37% hydrochloric acid gave a clean yellow solid (0.85 g), recrystallized from acetone/ethanol to give 33 as ochre/yellow crystals (0.76 g), m.p. 229-232°C. IR: 3400, 3280, 3100, 1625, 1580, 1535, 1335, 1290, 1250, 1150, 1120, 990, 980, 820, 700, 620  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (DMSO): 9.09 (s,  $\text{H}_5$ ), 9.07 (d,  $J = 2.80$  Hz,  $\text{H}_4'$ ), 8.87 (d,  $J = 2.80$  Hz,  $\text{H}_6'$ ), 8.45 (br s,  $-\text{NH}_2$ ), 4.75 (s,  $-\text{OCH}_3$ ).  $^{13}\text{C-NMR}$  (DMSO): 152.09 ( $\text{C}_7$ ), 144.25 ( $\text{C}_2'$ ), 140.79 ( $\text{C}_{3a}$ ), 138.42 ( $\text{C}_{7a}$ ), 133.60 ( $\text{C}_5'$ ), 132.80 ( $\text{C}_4$ ), 131.93 ( $\text{C}_3'$ ), 128.71 ( $\text{C}_6$ ), 128.21 ( $\text{C}_6'$ ), 126.69 ( $\text{C}_1'$ ), 125.43 ( $\text{C}_4'$ ), 124.44 ( $\text{C}_5$ ), 63.68 ( $\text{OCH}_3$ ). (Note: NMR spectra should be run on freshly prepared solutions, due to instability of 33 in this solvent: *vide infra*.)  $M/z$ : 420 (parent ion and base peak), 406, 405, 333, 328, 239, 209.

**Single-Crystal X-Ray Diffraction Analysis of  
2-(2'-Amino-3',5'-dinitrophenyl)-7-methoxy-4,6-  
dinitrobenzotriazole (33)**

$C_{13}H_8N_8O_9$ , F.W. = 420.3, monoclinic space group  $P2_1/c$ ,  $a = 7.190(2)$ ,  $b = 8.836(2)$ ,  $c = 25.555(6)$  Å,  $\beta = 94.39(2)^\circ$ ,  $V = 1618.7(7)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{\text{calc}} = 1.725$  mg mm<sup>-3</sup>,  $\lambda(\text{MoK}\alpha) = 0.71073$  Å,  $\mu = 0.149$  mm<sup>-1</sup>,  $F(000) = 856$ ,  $T = 294^\circ\text{K}$ .

A clear orange 0.010 x 0.15 x 0.33 mm crystal, in the shape of a prism, was used for data collection on an automated Siemens R3m/V diffractometer equipped with an incident beam monochromator. Lattice parameters were determined from 25 centered reflections within  $20 \leq 2\theta \leq 41^\circ$ . The data collection range of  $hkl$  was:  $0 \leq h \leq 7$ ,  $-2 \leq k \leq 9$ ,  $-27 \leq l \leq 27$ , with  $[(\sin \theta)/\lambda]_{\text{max}} = 0.54$ . Three standards, monitored after every 97 reflections, exhibited random variations with deviations up to  $\pm 2.0\%$  during the data collection. A set of 3272 reflections was collected in the  $\theta/2\theta$  scan mode, with scan width  $[2\theta(K\alpha_1) - 0.6]$  to  $[2\theta(K\alpha_2) + 0.6]^\circ$  and  $\omega$  scan rate (a function of count rate) from  $2.0^\circ/\text{min.}$  to  $8.37^\circ/\text{min.}$  There were 2114 unique reflections, and 1779 were observed with  $F_0 > 3\sigma(F_0)$ . The structure was solved and refined with aid of the SHELXTL system of programs (Reference 19). The full-matrix least-squares refinement varied 297 parameters: atom coordinates and anisotropic thermal parameters for all non-H atoms, atom coordinates and isotropic thermal parameters for the nonmethyl H atoms. Ideal methyl H atoms were included using a riding model (coordinate shifts of C applied to attached H atoms, C-H distances set to 0.96 Å, H angles idealized). One common  $U_{\text{iso}}(\text{H})$  was refined for the methyl hydrogen atoms.

Final residuals were  $R = 0.045$  and  $wR = 0.046$  with final difference Fourier excursions of 0.50 and  $-0.23$  eÅ<sup>-3</sup>. The largest difference peak was located in a cavity large enough to accommodate a water molecule, but if so, the occupancy was very low ( $<10\%$ ), so it was not reported. Crystallographic details are given in the Appendix.

A solution of **33** (0.10 g, 0.24 mmol) in DMSO (10 mL) was heated at  $80^\circ\text{C}$  overnight, and quenched in water (50 mL) to give a clear yellow solution. Extraction with dichloromethane (2 x 50 mL) and evaporation to dryness gave a yellow oil; dissolution in toluene (25 mL) and standing over the weekend gave a yellow solid (0.50 g), m.p.  $225\text{--}228^\circ\text{C}$  (dec), identified as **34**. IR: 3400, 3300, 3090, 1635, 1620, 1590, 1510, 1330, 1280, 920, 815, 600, 590 cm<sup>-1</sup>. <sup>1</sup>H-NMR (DMSO): 9.13 (s, H<sub>5</sub>), 8.97 (d,  $J = 2.80$  Hz, H<sub>4'</sub>), 8.85 (d,  $J = 2.80$  Hz, H<sub>6'</sub>), 8.81 (br s, -NH<sub>2</sub>), 6.47 (br s, -OH(?)), 2.52 (s, DMSO). <sup>13</sup>C-NMR (DMSO): 164.40 (C<sub>7</sub>), 143.98 (C<sub>7a</sub>), 143.12 (C<sub>2'</sub>), 140.92 (C<sub>3a</sub>), 133.69 (C<sub>5'</sub>), 131.93 (C<sub>6'</sub>), 130.36 (C<sub>4</sub>, C<sub>5</sub>), 126.76 (C<sub>1'</sub>), 125.09 (C<sub>6'</sub>), 123.54 (C<sub>4'</sub>), 117.36 (C<sub>6</sub>), 40.41 (DMSO).  $M/z$ : 406 (parent ion), 98, 90, 78 (base peak), 63.

**2-(2'-AMINO-3',5'-DINITROPHENYL)-7-AMINO-4,6-DINITROBENZOTRIAZOLE (35)**

2-(2'-Amino-3',5'-dinitrophenyl)-7-methoxy-4,6-dinitrobenzotriazole (33) (0.25 g, 0.6 mmol) was suspended in ethanol (50 mL) saturated at 0°C with ammonia, and the reaction mixture was heated under reflux overnight. Cooling and filtration gave a yellow solid (0.22 g, 91%), which was recrystallized from acetone to give 35 as a fine yellow solid (0.18 g, 74%), m.p. 340°C (dec.). IR: 3350, 3315, 3240, 3200, 1620, 1590, 1530, 1500, 1480, 1350, 1330, 1290, 1260, 1150, 570 cm<sup>-1</sup>. <sup>1</sup>H-NMR (DMSO): 9.50 (br s, -NH<sub>2</sub>), 9.05 (s, H<sub>5</sub>), 9.05 (d, J = 2.80 Hz, H<sub>4</sub>), 8.99 (d, J = 2.80 Hz, H<sub>6</sub>), 8.90 (br s, -NH<sub>2</sub>). <sup>13</sup>C-NMR (DMSO): 143.87 (C<sub>7</sub>), 142.47 (C<sub>2'</sub>), 138.91 (C<sub>3a</sub>), 137.89 (C<sub>7a</sub>), 133.63 (C<sub>5'</sub>), 132.49 (C<sub>3'</sub>), 126.57 (C<sub>5</sub>), 125.61 (C<sub>4</sub>), 125.07 (C<sub>6'</sub>), 124.15 (C<sub>1'</sub>), 124.00 (C<sub>4'</sub>), 122.85 (C<sub>6</sub>). M/z: 405 (parent ion), 375, 313, 253, 207, 44 (base peak).

**2-(2'-AMINO-3',5'-DINITROPHENYL)-7-NITROFUOXANO-[4,5-e]BENZOTRIAZOLE (36)**

2-(2'-Amino-3',5'-dinitrophenyl)-7-methoxy-4,6-dinitrobenzotriazole (33) (0.20 g, 0.48 mmol) was suspended in ethanol (50 mL), and sodium azide (0.20 g) was added. Thirty-seven percent hydrochloric acid (1 mL) was added, and the reaction mixture was heated under reflux for 6 h. A yellow solid (0.70 g) was filtered off and washed with ethanol. The mother liquors were evaporated, diluted with water (25 mL) and filtered to give a brown solid (0.03 g). The two fractions were combined (0.10 g, 52%), and purified by flash column chromatography (silica/ethyl acetate) to give a yellow solid recrystallized from ethanol to give 36 (0.06 g, 31%), m.p. 231-234°C (dec). IR: 3420, 3280, 1630, 1590, 1440, 1400, 1335, 1260, 1150, 1120, 970, 920, 740, 725 cm<sup>-1</sup>. <sup>1</sup>H-NMR (DMSO): 9.12 (s, H<sub>5</sub>), 8.97 (d, J = 2.80 Hz, H<sub>4'</sub>), 8.84 (d, J = 2.80 Hz, H<sub>6'</sub>), 8.81 (br s, -NH<sub>2</sub>). <sup>13</sup>C-NMR (DMSO): 164.62 (C<sub>6</sub>), 144.11 (C<sub>7a</sub>), 143.27 (C<sub>2'</sub>), 140.99 (C<sub>3a</sub>), 133.67 (C<sub>5'</sub>), 131.90 (C<sub>3'</sub>), 130.45 (C<sub>5</sub>), 130.34 (C<sub>4</sub>), 126.84 (C<sub>1'</sub>), 125.30 (C<sub>6'</sub>), 123.68 (C<sub>4'</sub>), 117.42 (C<sub>7</sub>).



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**Appendix**

**DETAILS OF SINGLE-CRYSTAL X-RAY STRUCTURE  
ANALYSIS OF 2-(2'-AMINO-3',5'-DINITROPHENYL)-  
7-METHOXY-4,6-DINITROBENZOTRIAZOLE**

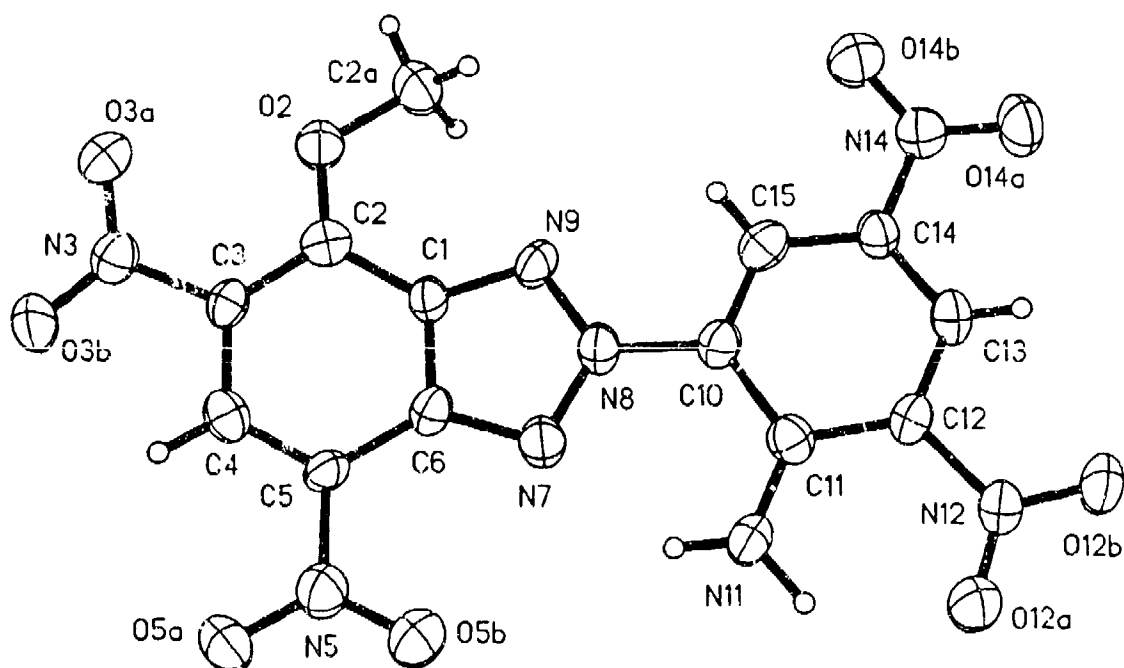


FIGURE A-1. Structure of 2-(2'-Amino-3',5'-dinitrophenyl)-7-methoxy-4,6-dinitrobenzotriazole.

TABLE A-1. Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Coefficients ( $\text{\AA}^2 \times 10^3$ ).<sup>a</sup>

	x	y	z	U(eq)
C(1)	3128(4)	1999(3)	3371(1)	31(1)
C(2)	2640(4)	3166(3)	2997(1)	32(1)
O(2)	3619(3)	3552(3)	2599(1)	46(1)
C(2A)	5259(5)	2706(5)	2479(1)	55(1)
C(3)	985(4)	3921(3)	3077(1)	31(1)
N(3)	303(4)	5180(3)	2741(1)	37(1)
O(3A)	1376(3)	5828(3)	2471(1)	51(1)
O(3B)	-1342(3)	5542(3)	2756(1)	53(1)
C(4)	-150(4)	3548(4)	3482(1)	35(1)
C(5)	332(4)	2441(3)	3835(1)	33(1)
N(5)	-860(4)	2133(3)	4254(1)	41(1)
O(5A)	-2375(3)	2770(3)	4243(1)	65(1)
O(5B)	-302(3)	1236(3)	4595(1)	57(1)
C(6)	2022(4)	1651(3)	3787(1)	31(1)
N(7)	2840(3)	545(3)	4075(1)	37(1)
N(8)	4388(3)	256(3)	3829(1)	35(1)
N(9)	4635(3)	1081(3)	3406(1)	37(1)
C(10)	5733(4)	-860(3)	4012(1)	33(1)
C(11)	5461(4)	-1753(3)	4471(1)	34(1)
N(11)	3976(4)	-1621(4)	4747(1)	43(1)
C(12)	6950(4)	-2793(3)	4605(1)	35(1)
N(12)	6926(4)	-3762(3)	5067(1)	42(1)
O(12A)	5931(3)	-3685(3)	5351(1)	57(1)
O(12B)	8225(3)	-4615(3)	5164(1)	77(1)
C(13)	8496(5)	-2927(4)	4326(1)	36(1)
C(14)	8650(4)	-2044(4)	3890(1)	35(1)
N(14)	10320(4)	-2162(3)	3605(1)	40(1)
O(14A)	11502(3)	-3105(3)	3749(1)	53(1)
O(14B)	10492(3)	-1294(3)	3236(1)	56(1)
C(15)	7282(4)	-1012(4)	3730(1)	36(1)

<sup>a</sup> Equivalent isotropic U defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

TABLE A-2. H-Atom Coordinates ( $\times 10^4$ ) and Isotropic Displacement Coefficients ( $\text{\AA}^2 \times 10^3$ ).

	x	y	z	U
H(2A)	5735	3147	2173	75(7)
H(2B)	4955	1665	2406	75(7)
H(2C)	6212	2750	2762	75(7)
H(4)	-1237(37)	4052(32)	3512(10)	32(8)
H(11A)	3847(45)	-2307(42)	5030(13)	65(11)
H(11B)	3155(46)	-881(42)	4652(13)	57(11)
H(13)	9383(36)	-3600(33)	4421(10)	29(8)
H(15)	7392(36)	-451(34)	3418(12)	39(9)

## NAWCWPNS TP 8211

TABLE A-3. Bond Lengths (Å) and Angles (°).

C(1)-C(2)	1.430 (4)	C(1)-C(6)	1.409 (4)
C(1)-N(9)	1.351 (4)	C(2)-O(2)	1.327 (4)
C(2)-C(3)	1.393 (4)	O(2)-C(2A)	1.449 (4)
C(3)-N(3)	1.467 (4)	C(3)-C(4)	1.406 (4)
N(3)-O(3A)	1.217 (4)	N(3)-O(3B)	1.229 (4)
C(4)-C(5)	1.356 (4)	C(5)-N(5)	1.448 (4)
C(5)-C(6)	1.415 (4)	N(5)-O(5A)	1.224 (4)
N(5)-O(5B)	1.224 (4)	C(6)-N(7)	1.334 (4)
N(7)-N(8)	1.345 (3)	N(8)-N(9)	1.326 (3)
N(8)-C(10)	1.434 (4)	C(10)-C(11)	1.439 (4)
C(10)-C(15)	1.378 (4)	C(11)-N(11)	1.333 (4)
C(11)-C(12)	1.429 (4)	C(12)-N(12)	1.460 (4)
C(12)-C(13)	1.370 (4)	N(12)-O(12A)	1.226 (4)
N(12)-O(12B)	1.211 (4)	C(13)-C(14)	1.372 (4)
C(14)-N(14)	1.455 (4)	C(14)-C(15)	1.380 (4)
N(14)-O(14A)	1.226 (4)	N(14)-O(14B)	1.229 (4)
C(2)-C(1)-C(6)	122.4(3)	C(2)-C(1)-N(9)	129.3(3)
C(6)-C(1)-N(9)	108.3(2)	C(1)-C(2)-O(2)	125.5(3)
C(1)-C(2)-C(3)	114.6(3)	O(2)-C(2)-C(3)	119.9(3)
C(2)-O(2)-C(2A)	121.2(2)	C(2)-C(3)-N(3)	121.9(3)
C(2)-C(3)-C(4)	123.1(3)	N(3)-C(3)-C(4)	115.0(3)
C(3)-N(3)-O(3A)	119.4(3)	C(3)-N(3)-O(3B)	117.3(2)
O(3A)-N(3)-O(3B)	123.3(3)	C(3)-C(4)-C(5)	121.6(3)
C(4)-C(5)-N(5)	119.4(3)	C(4)-C(5)-C(6)	118.4(3)
N(5)-C(5)-C(6)	122.2(3)	C(5)-N(5)-O(5A)	118.3(3)
C(5)-N(5)-O(5B)	118.0(3)	O(5A)-N(5)-O(5B)	123.7(3)
C(1)-C(6)-C(5)	119.7(3)	C(1)-C(6)-N(7)	109.1(2)
C(5)-C(6)-N(7)	131.2(3)	C(6)-N(7)-N(8)	103.1(2)
N(7)-N(8)-N(9)	116.4(2)	N(7)-N(8)-C(10)	122.7(2)
N(9)-N(8)-C(10)	120.9(2)	C(1)-N(9)-N(8)	103.2(2)
N(8)-C(10)-C(11)	120.9(2)	N(8)-C(10)-C(15)	116.7(3)
C(11)-C(10)-C(15)	122.4(3)	C(10)-C(11)-N(11)	123.1(3)
C(10)-C(11)-C(12)	113.8(3)	N(11)-C(11)-C(12)	123.0(3)
C(11)-C(12)-N(12)	121.0(3)	C(11)-C(12)-C(13)	123.5(3)
N(12)-C(12)-C(13)	115.5(3)	C(12)-N(12)-O(12A)	120.2(3)
C(12)-N(12)-O(12B)	118.3(3)	O(12A)-N(12)-O(12B)	121.5(3)
C(12)-C(13)-C(14)	119.5(3)	C(13)-C(14)-N(14)	119.1(3)
C(13)-C(14)-C(15)	121.1(3)	N(14)-C(14)-C(15)	119.7(3)
C(14)-N(14)-O(14A)	118.5(3)	C(14)-N(14)-O(14B)	118.3(3)
O(14A)-N(14)-O(14B)	123.1(3)	C(10)-C(15)-C(14)	119.7(3)

TABLE A-4. Anisotropic Displacement Coefficients ( $\text{\AA}^2 \times 10^3$ ).<sup>a</sup>

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
C(1)	33(2)	29(2)	31(2)	3(2)	1(1)	-2(1)
C(2)	35(2)	33(2)	28(2)	-5(2)	1(1)	0(2)
O(2)	44(1)	49(2)	47(1)	9(1)	15(1)	15(1)
C(2A)	45(2)	60(3)	63(2)	13(2)	17(2)	12(2)
C(3)	38(2)	25(2)	29(2)	2(2)	-3(1)	2(1)
N(3)	44(2)	34(2)	34(1)	2(1)	2(1)	2(1)
O(3A)	56(1)	44(2)	54(1)	-1(1)	11(1)	17(1)
O(3B)	44(1)	58(2)	57(1)	19(1)	5(1)	18(1)
C(4)	35(2)	32(2)	38(2)	5(2)	4(1)	-5(2)
C(5)	39(2)	31(2)	28(2)	3(2)	5(1)	3(1)
N(5)	43(2)	43(2)	37(2)	5(1)	7(1)	4(1)
O(5A)	52(2)	82(2)	65(2)	29(1)	26(1)	26(1)
O(5B)	64(2)	64(2)	45(1)	14(1)	13(1)	23(1)
C(6)	37(2)	29(2)	27(2)	4(2)	1(1)	-1(1)
N(7)	38(1)	38(2)	34(1)	5(1)	5(1)	4(1)
N(8)	35(1)	37(2)	33(1)	6(1)	2(1)	1(1)
N(9)	41(2)	38(2)	33(1)	6(1)	4(1)	7(1)
C(10)	34(2)	32(2)	32(2)	6(1)	-4(1)	1(1)
C(11)	36(2)	34(2)	32(2)	-1(2)	-1(1)	-1(2)
N(11)	43(2)	46(2)	40(2)	10(2)	9(1)	13(2)
C(12)	39(2)	32(2)	32(2)	3(2)	-1(1)	6(2)
N(12)	41(2)	43(2)	43(2)	7(1)	2(1)	9(1)
O(12A)	57(1)	65(2)	50(1)	19(1)	15(1)	19(1)
O(12B)	60(2)	93(2)	81(2)	40(2)	21(1)	52(2)
C(13)	38(2)	33(2)	38(2)	8(2)	-1(2)	1(2)
C(14)	35(2)	34(2)	35(2)	4(2)	1(1)	-4(2)
N(14)	42(2)	42(2)	38(2)	3(1)	2(1)	-3(2)
O(14A)	46(1)	59(2)	55(1)	19(1)	4(1)	3(1)
O(14B)	58(1)	59(2)	54(1)	7(1)	18(1)	15(1)
C(15)	42(2)	35(2)	30(2)	0(2)	2(1)	1(2)

<sup>a</sup> The anisotropic displacement factor exponent takes the form:  
 $-2\pi^2(h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12})$ .



## STRUCTURE DETERMINATION SUMMARY

## CRYSTAL DATA

Empirical Formula	$C_{13} H_8 N_8 O_9$
Color· Habit	
Crystal Size (mm)	0.10 x 0.13 x 0.33
Crystal System	Monoclinic
Space Group	$P2_1/c$
Unit Cell Dimensions	$a = 7.190(2) \text{ \AA}$ $b = 8.836(2) \text{ \AA}$ $c = 25.555(6) \text{ \AA}$ $\beta = 94.39(2)^\circ$
Volume	$1618.7(7) \text{ \AA}^3$
Z	4
Formula Weight	420.3
Density(calc.)	$1.725 \text{ Mg/m}^3$
Absorption Coefficient	$0.149 \text{ mm}^{-1}$
F(000)	856

## DATA COLLECTION

Diffractometer Used	Siemens R3m/V
Radiation	MoK $\alpha$ ( $\lambda$ = 0.71073 Å)
Temperature (K)	294
Monochromator	Highly oriented graphite crystal
2 $\theta$ Range	3.1 to 45.0°
Scan Type	Wyckoff
Scan Speed	Variable; 2.07 to 8.37°/min. in $\omega$
Scan Range ( $\omega$ )	1.20°
Background Measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 50.0% of total scan time
Standard Reflections	3 measured every 98 reflections
Index Ranges	$0 \leq h \leq 7$ , $-2 \leq k \leq 9$ $-27 \leq l \leq 27$
Reflections Collected	3272
Independent Reflections	2114 ( $R_{\text{int}}$ = 0.65%)
Observed Reflections	1779 ( $F > 3.0\sigma(F)$ )
Absorption Correction	N/A

## SOLUTION AND REFINEMENT

System Used	Siemens SHELXTL PLUS (VMS)
Solution	Direct Methods
Refinement Method	Full-Matrix Least-Squares
Quantity Minimized	$\sum w(F_o - F_c)^2$
Absolute Structure	N/A
Extinction Correction	$\chi = 0.0010(2)$ , where $F^* = F [ 1 + 0.002\chi F^2 / \sin(2\theta) ]^{-1/4}$
Hydrogen Atoms	Riding model, fixed isotropic U
Weighting Scheme	$w^{-1} = \sigma^2(F) + 0.0002F^2$
Number of Parameters Refined	297
Final R Indices (obs. data)	R = 4.52 %, wR = 4.60 %
R Indices (all data)	R = 5.56 %, wR = 4.74 %
Goodness-of-Fit	1.75
Largest and Mean $\Delta/\sigma$	0.004, 0.000
Data-to-Parameter Ratio	6.0:1
Largest Difference Peak	0.50 eÅ <sup>-3</sup>
Largest Difference Hole	-0.23 eÅ <sup>-3</sup>

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